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THE PHENOMENON OF SECONDARY PERIODICITY IN THE GROUP OF ELEMENTS OF THE ALKALI EARTH METALS

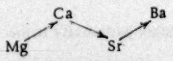
A.G. Bergman and N.A. Bychkova

The occurence of secondary periodicity in D.I. Mendeleev's table was observed for the first time by A.I. Bazarov in 1887 and was studied more closely by E.V. Biron [1] in 1915. The latter observed that secondary periodicity is particularly marked in the principal subgroups of the 5th, 6th and 7th groups, and most conspicuously of all in their oxygenated compounds. Thus, the heats of formation of the lower oxides show that Cl and I, S and Te, P and Sb have a greater affinity for oxygen than, respectively, Br, Se, As.

S.A. Shchukarev and I.V. Vasilkova [2] detected a periodicity of the change of heats of formation for compounds of the 4th group elements Si, Ge, Sn and Pb with magnesium. In the 3rd group secondary periodicity is insignificant, while in the 1st and 2nd groups it is scarcely manifested [1, 3].

Consideration of many properties of various elements led E.V. Biron [1] to the conclusion that in the earlier groups of the periodic system secondary periodicity is a rare phenomenon. In the 2nd group he only observed secondary periodicity in the zinc subgroup. Other authors likewise failed to detect such a periodicity in compounds of the alkali earth metals.

Our examination of the systems $MeO - SiO_2$, where Me is an alkali earth metal (Table 1), shows that the properties of the alkali earth metals in the main change monotonically in passage through the group from top to bottom, i.e. there is a gradual increase in the stability of the more acidic silicates from Be to Ba (with increasing basicity). Apart from this, however, a periodic change of properties of these elements is observed in the group in the same direction from Mg to Ba. This periodicity is reflected in the ability of the indicated elements to form sometimes fewer and sometimes more silicate compounds. Thus in the systems (Table 1) with participation of Mg and Sr only two compounds (each) are formed, while systems containing Ca and Ba give no fewer than 4 silicate compounds each. There is a periodic change (rise and fall) of the chemical activity of the alkali earth metals during formation of silicates in the direction from Mg to Ba: Ca and Ba manifest greater activity and Mg and Sr a lower activity. (Beryllium is not included in this series.) This may be represented schematically as follows:



This scheme reflects the periodic change of properties of elements in the group of the alkali earth metals or the phenomenon of secondary periodicity in this group of D.I. Mendeleev's table.

Secondary periodicity of the properties of elements in their compounds is due to the secondary periodicity of the properties of the free atoms, which is most clearly manifested in the periodic change of ionization potentials of elements in the groups in passing from top to bottom. Periodicity is manifested for potentials of higher orders close to the number of the group, i.e. when s-electrons are split off. However, the values of the ionization potentials of the alkali earth metals in the vertical direction of the group, even though they do not change monotonically, do not change with well-marked periodicity, as evident from the diagram.

Evidently this is also the cause of the absence of periodicity of change of properties of the alkali earth metals in the majority of compounds. An exception, however, is the silicates, in whose formation the alkali earth metals develop secondary periodicity. This anomalous behavior of the silicates is due to the greater complexity of the bond in these compounds in comparison with that in the normal simple compounds.

It is interesting that the formation of double salts from the chlorides of the alkali earth metals and KCl is also accompanied by periodicity of change of properties of the alkali earth metals in the vertical direction of the groups in the same order as in the formation of silicates (Table 2). But with Mg and Sr in this case there is a greater tendency to form double salts than with Ca and Ba, in contrast to the greater activity of Ca and Ba during formation of silicates. Possibly the characteristic bond in the double salts is also here responsible, since the pattern of development of periodicity by the alkali earth metals is the same as in the first-mentioned case but is expressed in a different form.

These examples of manifestation of secondary periodicity of the alkaline earth metals compel us to consider more

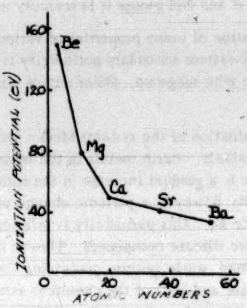
TABLE 1

System	Types of compounds					
	$3MeO \cdot SiO_2$	$2MeO \cdot SiO_2$	$3MeO \cdot 2SiO_2$	$MeO \cdot SiO_2$	$2MeO \cdot 3SiO_2$	$MeO \cdot 2SiO_2$
$BeO - SiO_2$	–	$2BeO \cdot SiO_2$	–	–	–	–
$MgO - SiO_2$	–	$2MgO \cdot SiO_2$ K.* 1890°	–	$MgO \cdot SiO_2$ I.** 1557°	–	–
$CaO - SiO_2$	$3CaO \cdot SiO_2$ In the solidus 1900-1250°	$2CaO \cdot SiO_2$ K. 2130°	$3CaO \cdot 2SiO_2$ I 1475°	$CaO \cdot SiO_2$ K. 1540°	–	–
$SrO - SiO_2$	–	$2SrO \cdot SiO_2$	–	$SrO \cdot SiO_2$ K. 1580°	–	–
$BaO - SiO_2$	–	$2BaO \cdot SiO_2$	–	$BaO \cdot SiO_2$ K. 1604°	$2BaO \cdot 3SiO_2$ K. 1450°	$BaO \cdot 2SiO_2$ I. 1420°

* K – compound melting without decomposition.
** I – compound melting with decomposition.

TABLE 2

System	Number of double salts	Double salts
$MgCl_2 - KCl$	2	$MgCl_2 \cdot KCl$, $MgCl_2 \cdot 2KCl$ (K.*)
$CaCl_2 - KCl$	1	$CaCl_2 \cdot KCl$ (K.)
$SrCl_2 - KCl$	2	$2SrCl_2 \cdot KCl$ (I.**) $SrCl_2 \cdot 2KCl$ (K.)
$BaCl_2 - KCl$	1	$BaCl_2 \cdot 2KCl$ (K.)



deeply the causes of the development of secondary periodicity in the Mendeleev table than do the previous data.

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Rostov-on-Don State University

A LABORATORY METHOD OF PREPARATION OF NITROGEN TRIOXIDE

P. I. Protsenko and V. B. Stradomsky

The method recommended by Laurie [1] for preparation of nitrogen trioxide is the passage of gaseous oxygen through liquid nitric oxide: $4NO + O_2 = 2N_2O_3$, or passage of gaseous nitric oxide through liquid nitrogen dioxide: $2NO + N_2O_4 = 2N_2O_3$.

It is easy to see that great difficulty would be experienced in carrying out these reactions even in a well-equipped laboratory. Moreover, these methods do not lead to pure nitrogen trioxide since it is not exactly easy to use the starting components in exactly the above-indicated stoichiometric quantities.

The method most commonly recommended for preparation of nitrogen trioxide is the reduction of nitric acid of specified concentration with arsenous oxide [2-5]. This method likewise does not ensure formation of pure nitrogen trioxide. It is also complicated by the difficulties associated with the use of arsenous oxide (toxicity and poor availability).

It is also impossible to obtain pure nitrogen trioxide by cooling a mixture of nitric oxide and nitrogen dioxide in equivalent amounts: $NO \quad NO_2 = N_2O_3$ It is extraordinarily difficult to maintain the amounts of oxides of nitrogen corresponding to the above stoichiometric equation, due to the ease of autoxidizability of nitric oxide, in consequence of which the resultant nitrogen trioxide is again impure. We must also assume that the inability to obtain the pure trioxide is the reason for the highly conflicting data on the properties of nitrogen trioxide in the literature.

Attention to this was even drawn by D.I. Mendeleev, who wrote: "Neither the anhydride nor the hydrate of the acid are known in the perfectly pure state. The anhydride has been obtained only as an extremely unstable substance, and has not been hitherto investigated with due completeness" [6]. The situation has changed but little since the days of D. I. Mendeleev.

We recommend a simple method of preparation of nitrogen trioxide which can be applied successfully both in laboratory practive and as a lecture experiment. The method is essentially based upon the known property of nitrates of easily decomposing under the action of concentrated sulfuric acid in accordance with the equation: $2NaNO_2 + H_2SO_4 = Na_2SO_4 + H_2O + N_2O_3$.

EXPERIMENTAL

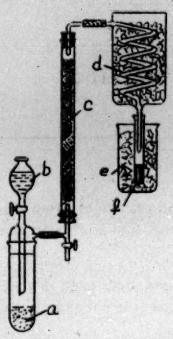
Previously dried, chemically pure sodium nitrite is introduced into a vessel shaped like a test tube (or into a round-bottomed flask) hermetically closed with a ground-glass stopper through which passes a sealed-in dropping funnel. Concentrated sulfuric acid is placed in the dropping funnel and run drop-wise into the reaction vessel. Evolution of a mixture of gaseous nitric oxide and gaseous nitrogen dioxide in equivalent amounts commences on addition of the first drops of acid. The reaction proceeds without application of heat.

The gases enter a drying tower filled with phosphorus pentoxide and glass wool. The dehydrated gas mixture passes through a glass coil cooled with solid carbon dioxide or a suitable cooling mixture, and is collected in a receiver also immersed in dry ice or freezing mixture (ice + salt).

The oxides of nitrogen start to condense 2 minutes after start-up of the reaction. After about 5 minutes, 2-2,5 ml liquid nitrogen trioxide with an intense blue color collects in a test tube with a diameter of 10 mm. Condensation of nitrogen trioxide takes place more slowly if the coil is cooled with a mixture of ice and salt.

In order to obtain pure nitrogen trioxide, the first portions of gases should not be condensed until the air has been displaced from the entire apparatus. It is recommended that the first portions of evolved gases be neutralized with caustic alkali solution. In addition all the connections in the apparatus must be of glass and well ground. It is also necessary to thoroughly to dry the mixture of gases by passage through two or three drying towers in series.

For prevention of formation of a "caked" mass of sodium sulfate in the reaction vessel which hinders the later uniform course of the reaction (when it is necessary to obtain large amounts of nitrogen trioxide), the sodium nitrite should be introduced into the reaction vessel in admixture with an equal volume of small glass beads (finely sliced glass rods).



Apparatus for preparation of N_2O_3. a) $NaNO_2$; b) conc. H_2SO_4; c) P_2O_5; d) solid carbon dioxide or ice-salt mixture; e) ice-salt mixture; f) N_2O_3.

The general set-up for a demonstration experiment on the preparation of nitrogen trioxide is shown in the diagram.

The proposed method of preparation of nitrogen trioxide has overwhelming advantages over the methods described in the literature, since it permits the liquefaction of the gases (without special regulation) in the equivalent amounts corresponding to the equation: $NO + NO_2 = N_2O_3$.

SUMMARY

A method is proposed for preparation of nitrogen trioxide by decomposing chemically pure sodium nitrite with concentrated sulfuric acid.

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Rostov-on-Don State University

THE COMPOSITION AND PROPERTIES OF BERYLLIUM BORIDES

L. Ya. Markovsky, Yu. D. Kondrashev and G.V. Kaputovskaya

In spite of the considerable research work in recent years on the chemistry of metallic borides [1-4] which has to a great extent filled the previous conspicuous gap in this field of chemistry, the system beryllium-boron has remained completely neglected. Up to recent times there were generally lacking any fully specific data on the composition of the borides of beryllium.

The first mention of a beryllium boride was made by Le beau [5] who obtained a crystalline substance insoluble in acids when he reduced beryllium oxide with amorphous boron in an electric furnace. He did not establish the composition of the substance. Since the reduction of BeO was effected in a carbon crucible, Lebeau assumed that the product also contained carbon.

On the other hand, Stock and Wiberg [6, 7] reported the existence of a beryllium boride soluble in acids and evolving boron hydrides during solution, in a similar manner to magnesium boride. They likewise did not give a chemical analysis. They did not isolate the beryllium boride in the pure form, but obtained it in admixture with BeO and B_2O_3 due to reduction of B_2O_3 by metallic Be. The best yield (judging by the evolution of boron hydrides) was got with a ratio by weight of $Be:B_2O_3 = 4:3$. Thus the literature data indicate the existence of at least two beryllium borides, one of which is soluble in acids, while the other is insoluble; no information has been published, however, about the composition and properties of these compounds.

Preliminary data for the composition of beryllium borides were recently published by the authors [8]. In the present paper they present supplementary data obtained in a study of the system beryllium-boron.

EXPERIMENTAL

Method of investigation. Samples of borides were prepared by synthesis from the elements in a hydrogen atmosphere and also in vacuum. Experiments in hydrogen were conducted in a tubular silite furnace in a quartz tube. The hydrogen was electrolytic material purified from traces of oxygen and moisture. The vacuum experiments were conducted in a TVV-2 vacuum furnace fabricated by the "Platinopribor" factory and with a residual pressure of the order of 5.10^{-3} mm.

Briqueted mixtures of pulverized beryllium and boron (pressure of approx. 800 kg/cm^2 during pressing), in the form of small cylinders with a diameter of 10 mm, were placed in the furnace in quartz test tubes or small crucibles lined with BeO.

Metallic beryllium used in the experiments was pulverized to a grain size of less than 0.1 mm and then contained (%): Be 97.8, Fe + Al 0.2, Si 0.4, insoluble residue 1.5.

The amorphous boron had the composition (%): B 96, Mg 1.4, Fe + Al 1.1, Si 0.3.

Chemical analysis of the prepared substances was performed mainly for determination of the Be and B contents*. The beryllium borides were brought into solution by prolonged decomposition with nitric acid in a flask fitted with a reflux condenser; the Be in the filtrate was determined in the form of BeO after distilling off the boric acid and carrying out two precipitations with ammonia; the boron was determined in another portion of solution after removal of the Be with the help of KOH. Boron hydrides in the gas phase were determined by absorption with concentrated caustic alkali solution.

X-ray examination of the samples was carried out with Fe_{K_α} - radiation in chambers with cell diameters of 57.3 and 143.25 mm.

Phase composition of products obtained by interaction of beryllium with boron

The phase composition was studied by X-ray investigation of briqueted mixtures of Be and B obtained after calcination at 1300° and 1400°. The mixtures examined were made up from molar ratios of Be:B equal to 20:1, 10:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1, 2:3, 2:5, 1:2, 1:4 and 1:6; in this connection it should be mentioned that these ratios varied slightly due to the volatility of the boron during calcination, as can be seen from the analyses set forth below (Tables 3 and 4).

* The boride samples were analyzed by A. G. Petrova.

TABLE 1

Phase Composition of Products of Reaction of Be with B at 1300-1400°

Expt. No.	Be : B molar ratio	Percent insoluble residue	Color of product	Phase composition on basis of X-ray analysis	Remarks
1	20:1	0.4	Metallic luster with very faint pink tinge*	Metallic Be + α phase	Ductile, but slightly brittle
2	10:1	0.9	Metallic luster with pink tinge		
3	6:1	7.1	Bronze-red	δ Phase	Compact, porous, brittle
4	5:1	7.1		δ Phase admixed with α	
5	4:1	8.0		δ Phase + α	
6	3:1	3.6	Copper red	α Phase + δ	
7	5:2	1.0-3.0		α Phase + trace of δ	
8	2:1	3-20	Copper red	α Phase + traces of β phase	Brittle, porous sinter
9	3:2	40	Bronze	α Phase + admixture of β	Compact, porous sinter
10	1:1	40-65	Color of brass	α Phase + admixture of β	Compact sinter with metallic appearance
11	2:3	83	Steel grey	β Phase + admixture of α	Hard and brittle, porous sinter
12	2:5	---		β Phase + traces of α phase	
13	1:2	70-90			
14	1:4	90-96	Brick red	γ Phase + admixture of β phase	Crumbly, soft, non-sintered product
15	1:6	90-96		γ Phase	

The data obtained indicate the occurrence in the system Be-B of three individual phases which differ markedly both in their X-ray diagrams (Fig. 1) and in their outward appearance and physical properties. In addition, lines of a fourth δ phase were detected on the X-ray diagrams in some experiments in mixtures rich in beryllium. In respect of X-ray characteristics this phase differed from the α phase, but it was very similar to the latter in chemical properties and outward appearance. The composition of this phase has not yet been established.

A difficulty in the way of identification of the prepared compounds was the presence in the majority of the prepared sinters of at least two phases at the same time. Some of the samples of borides also had a very small content of BeO.

The α boride phase and its properties

As follows from the data of Table 1, the lines of the α phase are obtained at Be:B ratios of 20:1, 10:1, 5:1, 5:2, 2:1, 1:1 and 3:2; traces of this phase also appear even at ratios of 1:2 and 2:5. The data of Table 2, obtained at a Be:B ratio of 2:1, show that traces of α phase are formed even at 1000°, while at 1100° the reaction between beryllium and boron proceeds to completion with formation of α phase, although at this temperature the final product also contains some β phase.

The purest specimens of α phase are obtained at lower temperatures; but even the purest specimens contain from 3 to 5% insoluble material consisting of another boride phase.

The α boride phase is actually completely soluble in acids; in dissolving it evolves boron hydrides, but the residue after dissolution does not exhibit the lines of this phase.

Dilute hydrochloric acid, both in the cold and on heating, completely dissolves the α boride phase. Slow hydrolysis of this boride even occurs in water in the cold with formation of boron hydrides and with separation of $Be(OH)_2$. The β and γ phases are insoluble in hydrochloric acid and do not evolve boron hydrides.

It follows from the data of Table 3, in which is also set forth (in experiment 9) the phase composition of beryllium boride prepared [6, 7] by reduction of B_2O_3 with metallic Be at a B_2O_3:Be ratio of 3:4, that this product likewise contains α phase.

* See data on metallography of alloys of beryllium with 6% boron [9].

TABLE 2

Phase composition of products of reaction of Be with B at various temperatures and at 2:1 molar ratio

Expt. No.	Reaction temperature	Phase composition of product on basis of X-ray data
1	1000°	Metallic beryllium + traces of α phase
2	1100	α phase in admixture with β phase
3	1200	
4	1250	
5	1300	
6	1350	
7	1400	α phase + β phase
8	1470	α phase + β phase

The X-ray analytical data show that the purest specimens of α phase are obtained at a Be:B ratio of 2:1. The chemical analyses set forth in Table 3 show, however, that in many of the specimens of boride containing α phase the ratio of Be:B >2.

The structural data submitted later and the crystal-chemical considerations also confirm that the α phase corresponds to the composition of Be_2B.

When decomposed with water and with acids, Be_2B evolves boron hydrides in amounts up to 4 wt.-% of the original weight of substance. Hydrogen is given off at the same time, indicating that a large proportion of the initially formed boron hydrides decomposes.

The amount of evolved hydrogen corresponds to approximately 2.5 moles H_2 per mole Be_2B, i.e. it corresponds to the following probable equation of hydrolysis:

$$2Be_2B + 9H_2O \rightarrow 4Be(OH)_2 + B_2O + 5H_2$$

TABLE 3

Data of chemical and phase analysis of boride compositions containing α phase

No.	Original molar ratios of Be:B	Reaction temperature	Percent of insoluble residue	Composition of soluble portion of boride (in %)			Be:B ratio in soluble portion of boride	Data of phase analysis	Density of sinter (g/cm³)	Hydrogen evolved per mole Be_2B
				Be	B in gas	B in filtrate				
1	2:1	1300°	3.0	62.5	1.3	33.2	2.17:1	α	2.156	2.58
									2.213	2.66
2	2:1	1300	18.5	50.2	1.5	31.3	1.93:1	α + admixed β	—	2.73
3	2.1	1450	32.1	42.4	1.5	19.3	2.18:1			
4	2.1	1200	35.5	43.1	0.7	20.9	2.39:1			
5	4.1	1540	55.2	26.7	3.7	14.8	1.73:1	α + β		2.52
6	5:2	1540	50.8	31.8	0.5	16.8	2.21:1	α + β	2.32	—
7	3:1	1300	6.7	66.8	—	26.9	2.98:1	α + δ	—	—
8	5:2	1300	12.5	61.7	1.1	15.5	2.79:1	α + δ	2.12	—
9	B_2O_3 + Be	—	—	—	—	—	—	α + BeO	—	—

TABLE 4

Specimen No.	Initial molar ratio of Be:B	Reaction temperature	Percent of insoluble residue	Composition of insoluble residue (in %)		Be:B ratio in insoluble portion of product according to analytical data
				Be	B	
1	1:1	1400°	40.5	28.5	71.2	1:2.07
2	1:2	1300	79.5	35.1	64.9	1:1.07
3	1:2	1400	86.5	27.8	72.2	1:2.03
4	1:2	1300	70.0	29.1	69.2	1:1.97
5	1:2	1450	88.7	32.6	67.2	1:1.85
6	2:1	1450	32.1	30.9	69.3	1:1.87

The boride Be_2B is obtained in the form of compact but porous sinters with a copper-red color. The density of the product at 20°, determined pycnometrically in benzene, varies between 2.15 and 2.22 g/cm³ depending upon the content of insoluble residue.

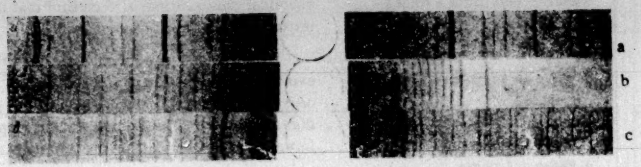

Fig. 1. X-ray diagrams of beryllium borides.
a - α phase; b - β phase; c - γ phase.

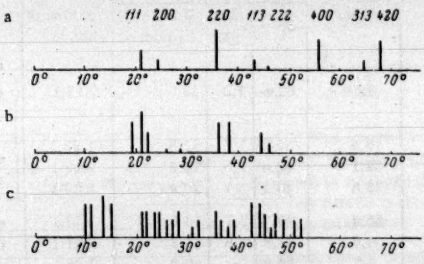

Fig. 2. Scheme of the X-ray diagrams of beryllium borides.
a - α phase b - β phase; c - γ phase.

The structure of this boride was established from powder diagrams of a sample containing 64.5% B (the theoretical values for Be_2B are 62.5% Be and 37.5%B) [8]. It is characterized by the following data: cubic system, size of cell a = 4.661 ± 0.001 kx, number of molecules in cell 4, $d_{x\text{-}ray}$ = 1.9 g/cm³. Space group O_h^5. Structure of the antitype of CaF_2.

The coordination of the beryllium atom is tetrahedral that of the boron is octahedral (at the vertices of a regular cube) the Be-Be distance is 2.33 A, the B-B distance is 3.30 A, and the Be-B distance is 2.01 A. The last distance is sufficiently close to the sums of the atomic radii of Be and B.

The X-ray diagram of Be_2B is represented in Fig. 1 and the details of the X-ray diagram in Fig. 2, a.

The structure found provides satisfactory agreement between the calculated and observed intensities of the lines [8]. The slight disparity is probably due to deviation of atoms from the neutral state assumed for the calculation. It is interesting that the structure of Be_2B is identical with the structure of Be_2C which indicates the crystallochemical similarity between these compounds.

A number of facts point to the occurrence of an extended field of homogeneity for the Be_2B phase. Thus, on the one hand, the experimental density values are considerably higher than those calculated from the X-ray data. On the other hand, for some specimens of this phase a weakening of the intensity is observed for lines with the sum of the indices multiplied by two but not by four, while the cell dimensions remain substantially unchanged. It may be suggested that this phenomenon is caused by a certain change of composition in the direction of a lower beryllium content, accompanied by an approach of the structure to the type of the cubic modification of ZnS. Due to the similarity in the atomic numbers of Be and B, this should result in an appreciable reduction in intensity of the lines with $h + k + l + 4n + 2$.

It should also be noted that the insoluble residue remaining after complete decomposition of Be_2B in acid in the majority of cases gives the lines of the β phase on the X-ray diagram; their chemical composition is also close to that of the β phase. Only in a single case were other lines detected in the insoluble residue. It is difficult to establish, however, whether they belong to a specific boride phase or to admixtures.

β phase. Conspicuous lines of this phase are observed in boride sinters prepared with Be:B ratios of 1:1, 2:3, 1:2 and 2:5, and even in compositions richer in boron (up to Be:B equal to 4) when the synthesis is carried out at a higher temperature.

As shown by experiments carried out with the specified ratios at various temperatures, the most intense and constant lines of the β phase are obtained at a Be:B ratio of 1:2, the lines of this phase remaining unchanged after treatment of the borides with hydrochloric acid.

On the other hand, chemical analysis of the insoluble residues obtained at various ratios of components (Table 4) also show the same ratio of 1:2. On the basis of these observations the β phase may be identified with the formula BeB_2.

Beryllium diboride has a dark-grey, almost steely color and is distinguished by great hardness and brittleness. Its density is 2.35 g/cm^3. This boride is easily oxidized by nitric acid and also by fused carbonates.

The scheme of the X-ray diagram of the diboride is detailed in Fig. 2 b.

γ phase. The lines of this phase are obtained in the X-ray diagrams of products synthesized at Be:B ratios of 1:4 and 1:6, but they are only adequately distinct with the latter ratio.

This fact, in association with the chemical analyses (Table 5), permits the assumption that the γ phase has the composition BeB_6.

TABLE 5

Chemical analyses of the boride γ phase

Specimen No	Initial molar ratio of Be:B	Percent of insoluble residue	Composition of insoluble residue (in %)		Theoretical requirement for BeB_6 (%)	
			Be	B	Be	B
1	1:4	96.3	9.8	90.2	12.4	87.6
2	1:6	91.5	10.5	89.5		
3	1:6	94.9	12.6	86.0		

TABLE 6

Initial composition Be : B	Specific electrical resistance Ω/cm^3
2:1	0.004
3:2	7.5
1:2	18.2
1:4	58.4
1:6	34.6

The γ phase differs markedly from the two preceding phases in external appearance since it is impossible to obtain a dense sinter at temperatures up to 1500°. The boride of this composition is always obtained in the form of a crumbly powder with a brick-red color, sometimes with a violet tinge. The density of the γ phase is 2.33 g/cm^3.

The γ phase is likewise insoluble both in water and in hydrochloric acid, but it is quickly decomposed by nitric acid. The scheme of the X-ray diagram of the γ phase is shown in Fig. 2, c.

Specific electrical resistance of the individual phases of beryllium borides

Preliminary characterization of the electrical properties of beryllium borides was effected by carrying out measurements of the specific electrical resistance of various specimens on a bridge of the Thomson-Wheatstone type.

For the measurements, small cylinders of boride sinters with a porosity of 45-50% were cleaned and polished before compressing in a hand press under gradually increasing pressure until the electrical resistance had a constant value. In some cases the specimens cracked during the measuring operation. In Table 6 are set forth the mean values obtained in the measurements, and it is seen that Be_2B possesses the lowest specific electrical resistance; subsequently, with

increasing percentage of boron the specific electrical resistance of boride sinters increases.

SUMMARY

1. Investigation of the system Be-B revealed the existence of three individual boride phases. The α phase was identified as Be_2B, which evolves boron hydrides when hydrolyzed. The structure and some physico-chemical properties of this boride were established.

2. The β and γ boride phases correspond to BeB_2 and BeB_6; they are insoluble in acids. Their structure has not yet been established.

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State Institute of Applied Chemistry

THE METANIOBATES OF CALCIUM AND BARIUM AND THEIR HYDRATES

E. I. Krylov and Yu. I. Alekseev

Statements in the literature indicate the possibility of obtaining metaniobates of the alkaline earth metals from aqueous solutions [1, 2]. Not one of the authors of the relevant papers, however, has succeded in preparing these salts in the pure form.

The literature does not contain any information about the preparation of the hydrates of metaniobates of the alkaline earth metals.

In the preceding communication we described a method of preparation and the properties of anhydrous strontium metaniobate $Sr(NbO_3)_2$ and its tetrahydrate $Sr(NbO_3)_2 \cdot 4H_2O$[3]. In the present work the method that we developed is applied to the preparation of the metaniobates of the remaining alkaline earth metals. In addition to the anhydrous salts $Ca(NbO_3)_2$ and $Ba(NbO_3)_2$, we have synthesized the dihydrate of calcium metaniobate $Ca(NbO_3)_2 \cdot 2H_2O$ and the trihydrate of barium metaniobate $Ba(NbO_3)_2 \cdot 3H_2O$, and we have studied some of their properties.

EXPERIMENTAL

1. Starting substances. The niobium pentoxide used in the present investigation was purified and analyzed by our previously described methods [3]. In addition, use was made in the investigation of the radioactive isotope of niobium Nb^{95} with a half-life of 37 days for determination of solubility. The potassium metaniobate required for synthesis of metaniobates of the alkaline earth metals was prepared by the method of A.V. Lapitsky [4], and was applied in solution in 1 N KOH. Solutions of calcium hydroxide and barium hydroxide were prepared as described in the literature [5]. The titer of the $Ca(OH)_2$ was equal to 0.092 g/ ml Ca^{++}, while that of $Ba(OH)_2$ was 0.0259 g/ ml Ba^{++}.

2. Preparation of hydrates of metaniobates of calcium and barium. The metaniobate of calcium (or barium) was precipitated after addition of the appropriate volume of standard solution of calicum (or barium) hydroxide to the calculated amount of potassium metaniobate dissolved in 1 N KOH: $Ca(OH)_{2\,aq} + 2KNbO_3 = Ca(NbO_3)_{2\,aq} + 2KOH$.

The resultant precipitate of calcium (or barium) metaniobate was filtered off, washed, and dried at 110°; it was then analyzed by the usual methods for its content of oxide of alkaline earth metal, niobium pentoxide and water of crystallization [6].

Results of the chemical analysis are set forth in Table 1.

TABLE 1

Chemical analysis of hydrates of metaniobates of calcium and barium (%)

Empirical formula	Oxide of alkaline earth metal		Niobium pentoxide		Water	
	Calc'd.	Found	Calc'd.	Found	Calc'd.	Found
$Ca(NbO_3)_2 \cdot 2H_2O$...	15.64	16.12	74.30	74.11	10.06	9.77
$Ba(NbO_3)_2 \cdot 3H_2O$...	32.34	32.12	56.24	56.63	11.42	11.25

The prepared salts $Ca(NbO_3)_2 \cdot 2H_2O$ and $Ba(NbO_3)_2 \cdot 3H_2O$ form white crystals poorly soluble in water.

3. Solubility of metaniobates of calcium and barium. A radiometric method was employed for determination of the solubility of the salts. For this purpose preparations of $Ca(NbO_3)_2 \cdot 2H_2O$ and $Ba(NbO_3)_2 \cdot 3H_2O$ were prepared which contained, in addition to ordinary niobium, the radioactive niobium isotope Nb^{95}; the latter has a simple β-spectrum accompanied by γ-radiation.

The activity was measured with reference to the γ-radiation with the help of a cylindrical glass counter in a type B apparatus. The procedure for determination of solubility was the same as previously [3]. The results are set forth in Table 2, which for comparison also includes data for strontium metaniobate.

4. Dehydration of the crystal hydrates $Ca(NbO_3)_2 \cdot 2H_2O$ and $Ba(NbO_3)_2 \cdot 3H_2O$. With the objective of establishing the composition and the number of intermediate crystal hydrates of calcium and barium metaniobates, we studied the process of dehydration at steadily rising temperatures, as previously described [3].

The curves of change of weight of the crystal hydrates of calcium and barium metaniobates in dependence upon the temperature and duration of dehydration are represented in Fig. 1.

TABLE 2

Solubility of hydrated metaniobates of the alkaline earth metals

Formula	Solubility at 15°		Solubility product
	g/liter	mole/liter	
$Ca(NbO_3)_2 \cdot 2H_2O$	0.00525	$1.47 \cdot 10^{-5}$	$1.26 \cdot 10^{-14}$
$Sr(NbO_3)_2 \cdot 4H_2O$	0.00607	$1.4 \cdot 10^{-5}$	$1.04 \cdot 10^{-14}$
$Ba(NbO_3)_2 \cdot 3H_2O$	0.00459	$0.974 \cdot 10^{-5}$	$3.65 \cdot 10^{-15}$

Examination of the dehydration curve of $Ca(NbO_3)_2 \cdot 2H_2O$ shows that this compound starts to appreciably dissociate at 136° with formation of the monohydrate $Ca(NbO_3)_2 \cdot H_2O$. The latter is stable in the range of 297 to 348°. Above 348° it rapidly dissociates with formation of anhydrous calcium metaniobate. The process of dehydration is complete at 483°.

When barium metaniobate trihydrate is heated above 110° it starts to lose two molecules of water with formation of the monohydrate $Ba(NbO_3)_2 \cdot 2H_2O$. The latter is stable between 228 and 254°. At 326° it is completely dissociated with formation of anhydrous barium metaniobate $Ba(NbO_3)_2$.

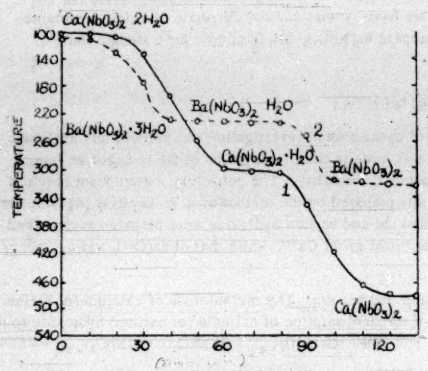

Fig. 1. Curves of dehydration of crystal hydrates. 1) $Ca(NbO_3)_2 \cdot 2H_2O$; 2) $Ba(NbO_3)_2 \cdot 3H_2O$.

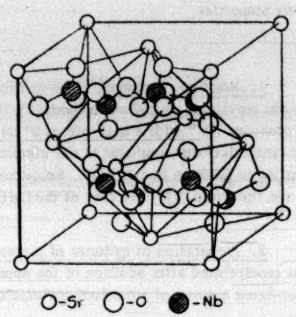

Fig. 2. Structure of metaniobate of strontium (calcium or barium).

5. X-ray investigation* of anhydrous metaniobates of calcium and barium and of their hydrates. Samples of all the compounds were obtained in the form of fine drystals and they were therefore examined by the powder method [7]. The X-ray photographs were taken with iron radiation in chambers with a cell diameter of 57.4 mm. The position of the lines on the X-ray diagram was determined to an accuracy of 0.2 mm. The intensity of the lines was evaluated visually on a five-point scale.

When investigating the structures of the metaniobates of calcium and barium it was assumed that these structures resembled the structure of $Sr(NbO_3)_2$ (Fig. 2). The latter compound forms a cubic face-centered lattice built up from Sr^{++} ions. Inside this lattice are distributed 8 NbO_3^- ions in the form of a plane triangle; the niobium atoms are not exactly in the center of the 8 octants, but considerably displaced. This lattice approximates to the fluorite type.

It was also assumed that the crystal hydrates $Ca(NbO_3)_2 \cdot 2H_2O$ and $Ba(NbO_3)_2 \cdot 3H_2O$ have the same structure as the anhydrous salts except that water of crystallization is located in the lattice voids.

The X-ray diagram was used for calculating the interplanar distances for all the compounds. Results of determination of the interplanar distances (d) in the crystals studied and the intensity (I) of the respective lines in the X-ray diagrams are set forth in Table 3.

The lattice parameters, calculated from all the lines of the X-ray diagrams are given in Table 4.

* With participation of Ael. K. Shtolts

TABLE 3

$Ca(NbO_3)_2$			$Ba(NbO_3)_2$			$Ca(NbO_3)_2 \cdot 2H_2O$			$Ba(NbO_3)_2 \cdot 3H_2O$		
Line No.	I	d (in A)	Line No.	I	d (in A)	Line No.	I	d (in A)	Line No.	I	d (in A)
1	Medium	4.83	1	Medium	3.90	1	Medium	3.74	1	Very weak	4.51
2	Very weak	3.42	2	Weak	3.10	2	Medium	3.43	2	Weak	4.06
3	Very weak	2.82	3	Weak	2.93	3	Weak	2.66	3	Very weak	3.68
4	Weak	2.31	4	Medium	2.77	4	Medium	2.42	4	Weak	3.19
5	Weak	2.24	5	Weak	2.44	5	Very weak	2.10	5	Medium	2.86
6	Weak	2.08	6	Weak	2.11	6	Weak	1.99	6	Weak	2.60
7	Medium	2.03	7	Medium	1.961	7	Weak	1.85	7	Weak	2.26
8	Weak	1.97	8	Weak	1.91	8	Medium	1.80	8	Medium	2.13
9	Medium	1.92	9	Very weak	1.79	9	Very weak	1.68	9	Weak	2.02
10	Weak	1.86	10	Medium	1.75	10	Very weak	1.451	10	Medium	1.93
11	Medium	1.78	11	Weak	1.69	11	Weak	1.401	11	Very weak	1.84
12	Medium	1.67	12	Medium	1.63	12	Medium	1.353	12	Very weak	1.82
13	Weak	1.63	13	Weak	1.60	13	Medium	1.280	13	Very weak	1.66
14	Weak	1.60	14	Very weak	1.56	14	Very weak	1.151	14	Very weak	1.65
15	Weak	1.475	15	Very weak	1.53	15	Weak	1.046	15	Very weak	1.55
16	Weak	1.437	16	Weak	1.457	16	Very weak	1.018	16	Weak	1.51
17	Weak	1.400	17	Very weak	1.395				17	Very weak	1.436
18	Weak	1.308	18	Very weak	1.374				18	Very weak	1.368
19	Very weak	1.266	19	Weak	1.350				19	Weak	1.335
20	Very weak	1.175	20	Weak	1.309				20	Very weak	1.297
21	Medium	1.140	21	Weak	1.262				21	Very weak	1.234
22	Medium	1.058	22	Weak	1.220				22	Very weak	1.172
23	Weak	1.045	23	Weak	1.198				23	Weak	1.115
24	Weak	1.034	24	Weak	1.190				24	Very weak	1.098
			25	Weak	1.166						
			26	Weak	1.096						
			27	Weak	1.088						

TABLE 4

Parameters of the crystal lattice

Compound	Lattice parameter (in A)
$Ca(NbO_3)_2$	8.35
$Sr(NbO_3)_2$	8.50
$Ba(NbO_3)_2$	8.77
$Ca(NbO_3)_2 \cdot 2H_2O$	8.41
$Sr(NbO_3)_2 \cdot 4H_2O$	8.56
$Ba(NbO_3)_2 \cdot 3H_2O$.....	9.02

On the basis of the above structure of the anhydrous metaniobates of the alkaline earth metals, and using the lattice parameters calculated from the data of the X-ray diagrams, we can determine the density of a compound [3] from the formula

$$\rho = \frac{n A_{mean}\, 1.65 \cdot 10^{-24}}{Q},$$

where n is the number of ions in the unit cell, A_{mean} is the mean atomic weight, and Q is the size of the unit cell, in A.

The densities of anhydrous metaniobates of the alkaline earth metals

TABLE 5

Density of anhydrous metaniobates of the alkaline earth metals

Compound	A_{mean}	n	Q	Density ρ (g/cm³) Calc'd from X-ray data	Density ρ (g/cm³) Experimental (pycnometric)
$Ca(NbO_3)_2$ ...	35.77	36	582.2	3.65	3.776
$Sr(NbO_3)_2$	41.05	36	614.1	3.97	3.886
$Ba(NbO_3)_2$.	46.55	36	674.5	4.09	4.046

TABLE 6

Melting points of the anhydrous metaniobates of the alkaline earth metals

Compound	Melting point
$Ca(NbO_3)_2$	1310° ± 20°
$Sr(NbO_3)_2$	1225 ± 20
$Ba(NbO_3)_2$	1285 ± 20

calculated in this way are set forth in Table 5 in which for comparison are included the pyknometrically determined values.

Toluene was used as the pyknometric liquid.

Comparison of these values may serve as confirmation of our hypothesis of the structure of the anhydrous metaniobates of the alkaline earth metals.

6. Melting point of the anhydrous metaniobates of the alkaline earth metals. The melting points of the anhydrous metaniobates of calcium and barium were determined from the cooling and heating curves using a platinum-platinum/rhodium thermocouple previously calibrated from the melting points of chemically pure salts: KNO_3, KCl, Na_2SO_4 and K_2SO_4. Results are set forth in Table 6.

SUMMARY

1. The preparation was effected of calcium metaniobate and its dihydrate $Ca(NbO_3)_2 \cdot 2H_2O$ and of barium metaniobate and its trihydrate $Ba(NbO_3)_2 \cdot 3H_2O$.

2. The existence of the monohydrates $Ca(NbO_3)_2 \cdot H_2O$ and $Ba(NbO_3)_2 \cdot 2H_2O$ was detected by the method of dehydration under continuous rise of temperature.

3. The solubilities of $Ca(NbO_3)_2 \cdot 2H_2O$ and $Ba(NbO_3)_2 \cdot 3H_2O$ at 15° were determined with the help of labeled niobium.

4. The roentgenographic method showed that the metaniobates of the alkaline earth metals form a cubic lattice of the fluorite type. The parameters of the crystal lattices for the anhydrous metaniobates of calcium and barium were determined and from these were obtained values of the densities of the compounds which were in satisfactory agreement with those determined pyknometrically (in toluene).

5. The melting points of the anhydrous metaniobates of calcium and barium were determined and found to be respectively 1310° ± 20° and 1285° ± 20°.

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S.M.Kirov Ural Polytechnic Institute

* T.p. = C.B. Translation pagination.

PARTICIPATION OF OXYGEN IN THE FORMATION OF ZINC SULFIDE LUMINOPHORS

N. Ril and G. Ortman

The presence of oxygen during preparation of zinc sulfide luminophors may have various effects: 1) The oxygen may play a certain part in reactions associated with the action of fluxes: 2) it may enter into the prepared luminophor as a component amenable to analytical determination: and 3) it may be a component of the centers of luminescence themselves.

1. Influence of oxygen on the action of halide fluxes

Many samples were found to show an extremely large deviation of the Zn:S ratio from the stoichiometric ratio, ranging up to several percent. Since these deviations depended upon the special conditions of preparation of the sample of luminophor, a study was made of the dependence of composition on the presence of atmospheric oxygen, on known additions of zinc oxide or sulfur, and on the conditions of calcination. To be able, however, to establish any regularities, it was necessary in the first place to investigate the mechanism of the action of the fluxes nearly always used in the calcination of ZnS luminophors [9].

In experiments designed for clarification of the role of the flux, use was made for the sake of simplicity not of the mixtures of various chlorides used in industry, but only of NaCl. Analysis of the batch after calcination at 700° in a crucible closed with an ordinary stopper always showed a certain content of $ZnCl_2$. Formation of the latter in the ignited batch has been known in itself for a long time, but the usual opinion that $ZnCl_2$ is formed as a result of direct reaction between ZnS and NaCl [1] appeared inapplicable in the present case since the calcination was deliberately conducted at a relatively low temperature (700°) *. According to Houben [2] only 0.1% zinc sulfide dissolves in fused NaCl at 870°: we ourselves found up to 1.5% zinc chloride in batches calcined only at 700°. In this connection the question arises whether some side or intermediate reactions may accompany the formation of $ZnCl_2$ from ZnS and NaCl. For the purpose of systematic study of the reactions, calcination was performed in a small boat in a quartz tube in order to trap and examine the gases given off. Although the calcination was conducted in a stream of inert gas (nitrogen or argon), a certain amount of SO_2 was always detected in the evolved gases. An approximate calculation showed that traces of oxygen present in the "inert" gas were sufficient to account for the amount of SO_2 found. The amount of SO_2 formed was then deliberately increased by calcining a mixture of ZnS and NaCl not in an inert gas but in a stream of air. After 2 hours' calcination at 700°, more than 50% of the total chlorine contained in the batch had disappeared and was found in the evolved gases (the ZnS was completely converted into ZnO). Calcination of the sulfide was accompanied by decomposition of the added NaCl. The volatility of NaCl at 700° is still very slight; even at 800° the vapor pressure is only 0.04 mm.**

A study was then made of the behavior of NaCl (without ZnS) at 700° in a stream of $SO_2 + O_2$. After 2 hours' calcination the trap through which the evolved gases passed contained much chlorine, while an amount of Na_2SO_4 exactly corresponding to the amount of gaseous chlorine was formed in the small boat.

The reaction here taking place:

$$2NaCl + SO_2 + O_2 \rightarrow Cl_2 (\uparrow) + Na_2SO_4 \qquad (1)$$

has long been known as one of the main reactions of the metallurgical process known as chlorinating roasting [5]. This process consists in roasting sulfide ores in presence of chlorides (NaCl), the sulfur dioxide formed releasing chlorine which chlorinates the sulfide ore.

The overall balance of these reactions is:

$$ZnS + 2NaCl + 2O_2 \rightarrow ZnCl_2 + Na_2SO_4. \qquad (2)$$

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* NaCl does not yet melt at 700°. Nevertheless considerable sintering of the batch takes place, which is evidence of formation of the readily fusible $ZnCl_2$.

** At 700° dry NaCl does not give gaseous chlorine; reports in the older literature [3] of the evolution of gaseous chlorine were due to the presence of water vapor, which on reaction with NaCl at 700° forms HCl (and the non-volatile residue gives an alkaline reaction [4].

As found in our experiments, the same reaction takes place also during preparation of ZnS luminophors (since calcination proceeds in presence of oxygen). The sulfur dioxide formed during partial roasting sets free chlorine from NaCl according to equation (1), and this chlorine chlorinates part of the zinc sulfide with formation of $ZnCl_2$.

Reaction (1) is by no means the sole possibility of liberation of chlorine from chloride fluxes. It was found that the quantity of gaseous chlorine fluctuated sharply from experiment to experiment if we used zinc sulfide from different sources.* Analyses of zinc sulfides from various sources revealed considerable variations in water content. A higher water content resulted in increased evolution of gaseous chlorine from the flux. This signifies that the water retained by the precipitated zinc sulfide takes part even at high temperatures in the formation of gaseous chlorine.

The role of the water is understandable from the reaction between H_2O and NaCl:

$$NaCl + H_2O \rightleftharpoons HCl(\uparrow) + NaOH.$$

Here the chlorine is freed in the form of HCl and can exert a chlorinating action on ZnS. If oxygen is present (and consequently also SO_2), then the NaOH formed according to equation (3) is consumed in neutralizing the SO_2:

$$2NaOH + SO_2(+O) \longrightarrow Na_2SO_3(Na_2SO_4) + H_2O.$$

The conjunction of reactions (3) and (4) gives the overall reaction:

$$2NaCl + SO_2 + H_2O + O \longrightarrow Na_2SO_4 + 2HCl(\uparrow).$$

Reaction (5) has likewise been known for a long time in industry under the name of the Hargreave process [5] for production of HCl and Na_2SO_4. Of significance for our problem is the fact that it proceeds even at 420-450° and with very small contents of SO_2. The HCl formed in the Hargreave reaction acts upon the ZnS and partly chlorinates it with formation of $ZnCl_2$.

The hydrogen sulfide formed during chlorination of zinc sulfide with hydrochloric acid can (in presence of oxygen) be oxidized and again provide SO_2 and H_2O for the Hargreave reaction. The water is thus regenerated, due to which even traces of H_2O in the sulfide suffice to bring about the Hargreave reaction under the conditions considered by us.

All these reactions can only take place in presence of oxygen. But even when the preparation of the luminophor is conducted in a stream of ordinary ** inert gas, the amount of oxygen introduced with the gas stream is found to fully suffice to make these reactions possible. Apart from that, the precipitated zinc sulfide itself contains a considerable amount of oxygen. An important source of oxygen is also the $ZnSO_4$ retained by the zinc sulfide precipitated from sulfuric acid solution; hydrate water is another source.

The initial problem was to limit the action of oxygen and in turn the formation of $ZnCl_2$ in order to influence the degree of crystallization and the luminescent properties of ZnS luminophors. For this purpose we started with zinc sulfide free from oxygen and water,*** mixed it (without access of atmospheric moisture) with pulverized NaCl which had previously been dehydrated by fusion, and charged the mixture into a quartz crucible fitted with a carefully ground cover. After calcination (at 700°) it was found that the charge had not sintered. Analysis of the wash liquor revealed almost complete absence of $ZnCl_2$. **** In view of the fact that there was substantially no crystallization of the sulfide, ***** the luminescence of the prepared product was negligible. But if the calcination was performed (under otherwise identical conditions) at a higher temperature (above 700°), then $ZnCl_2$ formation was also observed as well as crystallization, and the final product had a blue luminescence Formation of $ZnCl_2$ is evidently a decisive sign of formation of crystalline and luminescent zinc sulfide. Experiments of a similar type were carried out with the same result not only on activator-free ZnS but also on ZnSCu.

It may be suggested that the enhanced luminescence when $ZnCl_2$ is formed in the charge is based on the fact that $ZnCl_2$ as a low-melting salt is a particularly good mineralizer and exercises a solvent action upon the sulfide. In order to test this hypothesis we calcined pure ZnS at 700° in admixture with 2% $ZnCl_2$ as fluxing agent while observing all the above-noted precautions against access of oxygen. The brightness of the resultant luminophor proved negligible in comparison with the luminophor prepared at 700° with NaCl as the fluxing agent.******

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* In other words when variations occured in the conditions of precipitation, washing and drying of the zinc sulfide used.

** Not spectrally pure.

*** For this purpose the precipitated ZnS was subjected to previous calcination in a stream of H_2S at 500°.

**** Parallel experiments under the usual conditions (i.e. in presence of oxygen) gave 0.2-1% $ZnCl_2$ (on the weight of the charge) after calcination at 700°.

***** Sulfide suspended in water was precipitated only after several hours.

****** Completely non-luminescent preparations were obtained at 700° in the entire absence of a fluxing agent.

The prepared luminophor was moreover extremely finely dispersed, i.e. crystallization had been very incomplete.* Thus the favorable effect of chlorination of the sulfide is by no means accounted for by the action of the formed $ZnCl_2$ as such. We are of the opinion that the very process of chlorination is a mineralizing factor,** and that it promotes in some fashion also the formation of centers of luminescence.

2. Oxygen as a macrocomponent of ZnS luminophors amenable to analytical determination

In Table 1 are set forth the results of analyses of various types of ZnS luminophors.*** It is very obvious that in the majority of preparations there are considerable deviations of the content of zinc and sulfur from the stoichiometric amounts. We shall first consider the causes of these deviations, applying the foregoing considerations on the chemical functions of the fluxing agents.

TABLE 1

Results of analysis of some zinc sulfide luminophors

Luminophor No.	Luminophor characteristic	Content of Zn + S (%)	Deficiency of sulfur in relation to zinc (%)
1	Activator-free ZnS obtained at 850°	97.2	8.3
2	ZnSCu with 10^{-4} g Cu obtained at 850° with addition of free sulfur to the charge	98.4	0.9
3	The same with addition of 5% ZnO (in place of sulfur) to the charge	96.0	9.2
4	ZnSCu with 10^{-4} g Cu (technical product intended for radioactive luminescent compounds)	99.9	0
5	ZnSCu with 10^{-4} g Cu (technical product intended for ratioactive luminescent compounds)	100.0	0
6	ZnSCu with 10^{-4} g Cu (technical product with especially prolonged phosphorescence)	99.1	2.7
7	ZnSCu with 10^{-4} g Cu (technical product with especially prolonged phosphorescence)	99.0	1.5
8	ZnSCu with 10^{-4} g Cu prepared at 850° with 5% NaCl as flux	98.95	3.9
9	The same after lixiviation with acetic acid	100.0	0
10	ZnSCu with 10^{-4} g Cu prepared at 850° with 5% NaCl as flux and with 5% ZnO in the charge	98.9	5.7
11	The same after lixiviation with acetic acid	99.9	0
12	ZnSCu prepared at 850° from 100% sulfide prepared at 500° in a stream of H_2S; fluxed with 5% NaCl	100.1	0

Some of the foreign substances detected in luminophors and responsible for deviation from the formula ZnS apparently do not play a special part in the luminescent peroperties. If, for example, $BaCl_2$ was used during preparation apart from other chlorides, then formation was observed of $BaSO_4$ which was not washed out of the calcined luminophor and remained to influence the balance of the analysis. This was the case with luminophors numbers 1, 2, 3 and 7**** (Table 1).

A decisive part both for the balance of the reaction and for the luminescent properties is played by zinc oxide, which is formed during calcination due to partial roasting of the zinc sulfide, during hydrolysis of the precipitated sulfide, during drying and decomposition of oxygen-containing admixtures (for example $ZnSO_4$ which is present in the sulfide precipitated from sulfate solution). Moreover the prepared luminophor still contains (even with the most thorough washing after calcination) small amounts of Cl^-, Na^+, SO_4^{--} and other impurities from the flux or from the precipitated sulfide. The content of ZnO, apart from the dependence on the extent of access of air (i.e. on the efficiency of the closure of the crucible),

* We may note that, in contrast to the weak mineralizing action of zinc chloride, sodium chloride in presence of air at 700° has a marked mineralizing action even when the amount of NaCl added to the sulfide does not exceed 0.2 %.

** Compare previous observations on the mineralizing action of various gases on ZnS [6].

*** In the absence of special indications, the composition of the flux was the sameas in papers [7, 8].

**** The sulfur contained in $BaSO_4$ was deducted in calculating the contents of sulfur given in Table 1.

also depends markedly on the conditions of preparation of the original precipitated zinc sulfide. We therefore also carried out careful analysis of a precipitated zinc sulfide obtained under various conditions of precipitation. Although we analyzed those grades of precipitated zinc sulfide which are used for the preparation of high-quality, technically applicable luminophors, it was nevertheless found that nearly all the grades of precipitated sulfide deviated greatly from the theoretical stoichiometric composition (Table 2).

On the basis of the analyses of precipitated zinc sulfides set forth in Table 2, it becomes understandable why the content of ZnO in the finished luminophor was subjected to such wide fluctuations. Moreover, these analyses give an indication of the amounts of oxygen in the precipitated zinc sulfide. The amount of oxygen is so large that even with ideally efficient closure of the calcination crucible or with calcination in a stream of purest inert gas, oxygen can exercise the influence discussed above.

TABLE 2

Results of analyses of some types of "crude" zinc sulfide serving for preparation of ZnS luminophors

Characteristics of zinc sulfide (precipitated, uncalcined "crude" sulfide)	Content			
	ZnS	$ZnSO_4$	$ZnCl_2$	H_2O
Washed product of unknown origin	89.7	3.5	2.4	4.4
Sulfide obtained by precipitation from sulfate solution (final concentration of H_2SO_4 7%)	96.8	1.9	0	1.3
Sulfide obtained by precipitation from chloride solution (final concentration of HCl 3%)	93.6	0.2	2.8	3.4
Sulfide from sulfate solution after action of H_2S at 500°	100.0	0	0	0

In the preparation of high-quality ZnSCu luminophors for radioactive luminous compositions (compositions with "constant action"), special measures are taken against formation of ZnO.* Luminophors of this type are included in Table 1 (4 and 5). They differ conspicuously from the other luminophors in that the sum of their zinc and sulfur contents is 100%.

In contrast to this, the luminophors with exceptionally prolonged phosphoresence (numbers 6 and 7, Table 1) contain a considerable amount of ZnO which affects the Zn:S ratio. A high ZnO content is also to be expected in these luminophors, since in their preparation either ZnO is added to the charge or calcination is deliberately effected with limited access of air for the sake of enhancing the luminescence. This type of ZnSCu luminophors has a yellowish-green luminescence in contrast to the pure green of ZnSCu luminophors which are completely free from zinc oxide.**

On lixiviation with 5-10% acetic acid, the whole of the zinc oxide passes into solution since analysis of the residual luminophor gives a Zn:S ratio exactly corresponding to the formula ZnS (Table 1 and 3). Such a lixiviation of the ZnO, however, is only possible with those ZnS luminophors which have been calcined at not higher than 1050°.***

Acetic acid scarcely leaches out the zinc oxide from preparations calcined at temperatures above 1050°. (Such preparations are detailed in Table 1— luminophors 6 and 7, and also 4 and 5.) The hypothesis was advanced that zinc oxide is not removed from these preparations because of the following reaction (mentioned in the literature) between ZnO and ZnS at a high temperature:

$$ZnS + 2ZnO \longrightarrow 3ZnO(\uparrow) + SO_2(\uparrow). \qquad (6)$$

A check of this reaction during the ordinary preparative calcination of zinc sulfide in presence of a flux (NaCl) showed that it does not take place to an analytically detectable extent.

Consequently the strongly calcined ZnS luminophors can also contain large amounts of ZnO (this is also evident from the direct analysis of luminophors 6 and 7 in Table 1), but their ZnO is in a form which resists lixiviation. On the other hand it is precisely in such strongly calcined preparations that we observe the clear influence of the ZnO

* One such measure, for example, is inclusion of elemental sulfur in the charge.

** These differences and criteria relate only to technically high-grade preparations obtained by high-temperature calcination.

*** Leaching out of the oxide from such preparations does not alter their excitation in the long-wave ultraviolet, even though zinc oxide absorbs very strongly in this region of the ultraviolet (with mechanical mixing-in of t the non-luminescing zinc oxide, the excitability is markedly reduced). It might be suggested that the zinc oxide contained in a ZnS luminophor is itself a source of luminescence (and thereby compensates for the fall in brillance), since zinc oxide is known as a green-luminescing luminophor [9], but in that event the spectrum ought to change markedly after leaching-out of the oxide in the case of non-activated ZnS luminophors possessing a blue luminescence, whereas such a change does not occur. At all events it is impossible to regard the zinc oxide as being in a simple mechanical admixture.

content on the luminescent properties. All these facts point to a closer relation between the content of ZnO and the luminescent properties of ZnS luminophors than would correspond to the zinc oxide being present merely as "inert ballast". We may also recall that at temperatures above 1050°, ZnS has the wurtzite lattice, i.e. the same type of lattice as ZnO. It is probable that at temperatures above 1050° ZnO forms true "mixed substitution crystals" with ZnS.

TABLE 3

Results of lixiviation of a calcined charge with water and acetic acid

Luminophor No.	Characteristic of luminophor	Amount of zinc passing into solution during lixiviation	
		of calcined charge wtih water (% of lixiviated product)	of product subjected to preliminary leaching with water and acetic acid (% of product leached out by water)
1	ZnSCu with 10^{-4} g Cu prepared at 850°	2.39	1.96
2	The same (another portion)	1.42	1.72
3	The same as no. 1 but with addition of 10% sulfur to the charge	1.43	0.2
4	The same as no. 1 but with addition of 5% ZnO to the charge	1.23	6.6
5	Same as no. 1 but with a tightly closed crucible during calcination	1.65	4.1
6	ZnSCu with 10^{-4} g Cu prepared at 850° from a sulfide containing 0.2% sulfate	0.88	0.15
7	ZnSCu with 10^{-4} g Cu prepared at 850° from 100% zinc sulfide obtained at 500° in a hydrogen stream (see Table 2)	0.3	0.09

3. Participation of oxygen in the structure of the luminescent centers

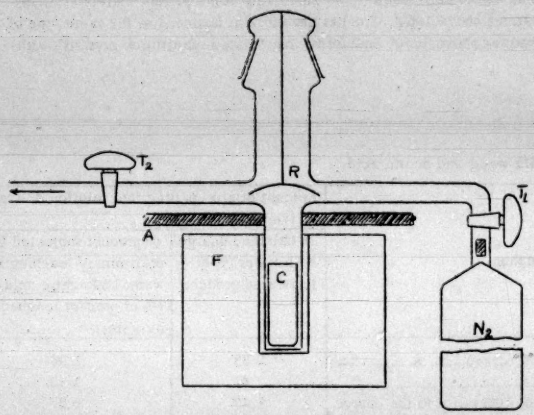
In order to establish whether oxygen can be a component of the luminescent center, we carried out the preparation of an activator-free ZnS luminophor under conditions excluding all possibility of the presence of oxygen. *

We started from precipitated zinc sulfide which had been subjected to calcination in a stream of H_2S at 500°. As already mentioned above, sulfide treated in this way should not contain oxygen in any form whatsoever. Immediately after conclusion of the treatment, this sulfide was mixed in a H_2S stream with 5% NaCl (previously dehydrated), charged into a crucible, and placed in the vacuum apparatus. Further thorough dehydration and elimination of occluded gases was then effected by gradual heating of the charge in vacuum (10^{-5} mm) and maintenance at 300° for 2 hours. A Bodenstein valve was then broken and connection was established with a glass cylinder containing spectrally pure nitrogen. Since the volume of that portion of the vacuum apparatus which contained the crucible was about 200 ml, and the volume of the nitrogen cylinder was 2 liters, this procedure was repeated several times with the help of taps T_1 and T_2, i.e. the nitrogen-filled apparatus was again evacuated, refilled with nitrogen, and so on. Finally a nitrogen pressure of about 0.8 atm. was created in the apparatus. Here it is necessary to point out that for absolute avoidance of access of oxygen, operations should be conducted not in a stream of inert gas but by a static method with a small free volume. After the above preliminary operations the charge was calcined at 1000°.

With strict observance of the specified experimental conditions, final products without blue luminescence were obtained.

If the slightest trace of oxygen happened to enter the apparatus (in such amount that the number of atoms of oxygen was of the same order as the number of luminescent centers in the zinc sulfide), then a blue luminescence at once appeared. An effect is consequently exercised by "microscopic" amounts of oxygen comparable (in respect of the number of atoms) with the number of centers of blue luminescence. In the absence of these exceedingly small

* This experiment must not be confused with the "oxygenless" experiment described earlier. In the latter a study was made only of the influence of oxygen upon the effectiveness of the flux as a mineralizer. At temperatures of the order of 700° crystallization and luminescence of the preparation occur only if oxygen is present. But at higher temperatures (1000° and above) crystallization also proceeded without participation of oxygen.



Vacuum apparatus for experiments in the complete absence of oxygen.
F - electric furnace; C - quartz crucible; A - asbestos plate; R - reflector; N_2 - glass cylinder containing spectrally pure nitrogen.

amounts of oxygen a blue luminescence of the activator-free zinc sulfide was never developed.

It should be noted that in experiments carried out in the absence of oxygen, definite thermal dissociation of the zinc sulfide was always observed; at a certain distance from the calcination section of the apparatus a black coating of metallic zinc was deposited, and some distance further away appeared a deposit of sulfur. The volatilized zinc caused an additional elimination of oxygen. The zinc sulfide in the crucible itself remained white, i.e. it did not contain large amounts of excess zinc.

It can be claimed that the experiments supply direct proof of the need for the presence of oxygen for formation of centers of blue luminescence in activator-free zinc sulfide. An interesting question, however, is whether oxygen is a component of the center of luminescence. It was established above that oxygen can play an important part as a promoter of the action of the flux, and it is impossible to reject the occurrence in this experiment of some indirect action of oxygen, particularly in presence of a chloride flux. It is true that the crystallization which took place was evidence on the other hand that the chloride flux also fulfilled its function in the absence of oxygen. The problem was investigated more closely by experiments to test whether in the complete absence of oxygen a non-luminescent preparation is also obtained when an activator (Cu) is present.

Two different methods were used. First, copper (10^{-4} g Cu per 1 g ZnS) was added to the crude zinc sulfide even before treatment of the sulfide in a stream of H_2S, and calcination was carried out in the absence of oxygen. Secondly, the copper was given an opportunity of diffusing at 450° into the finished non-luminescent preparation which had been calcined in absence of oxygen. In the second case the quantity of copper was 10^{-5} g Cu per 1 g ZnS.

In both cases a conspicuously luminescent luminophor was obtained. The brightness of luminescence did not differ from that of normal ZnSCu luminophors. Diffusion of 10^{-5} g Cu per 1 g ZnS gave a green luminescence, while the introduction of 10^{-4} g Cu per 1 g ZnS (added to the preparation) gave a bluish-green luminescence.

On the basis of the foregoing experiments we can conclude that the presence of traces of oxygen is not essential for formation of a ZnSCu luminophor, although activator-free zinc sulfide in the absence of oxygen is incapable of giving a blue luminescence. In other words, oxygen-free ZnSCu luminophors exist but oxygen-free activator-free ZnS luminophors do not exist.

An additional series of experiments was carried out by a different method. Precipitated ZnS, freed from oxygenated impurities in a stream of H_2S at 500°, was mixed with 5% NaCl and calcined for an hour in a stream of H_2S at 1000°. No activator was added. An activator-free zinc sulfide without blue luminescence was obtained (also free from any other luminescence). Addition of copper to the sulfide led to a normal ZnSCu luminophor. The same result was also obtained on diffusion of copper at 450° into the finished non-luminescing product.

Calcination of a mixture of ZnS and NaCl in an H_2S atmosphere at 1000° gave a considerable amount of HCl due to reaction between H_2S and NaCl. (We found the equivalent amount of Na_2S in the residual product*) This experiment is particularly significant since due to the formation of HCl the probability of reaction of chlorine with ZnS is incontestable. Due, however, to the absence of oxygen, a blue luminescence was not developed in spite of the presence of HCl. This conclusively removes any doubt as to whether during operation in vacuum the essential factor was the absence of the action of oxygen as a promoter of the formation of HCl.

SUMMARY

1. Oxygen participates in the formation of centers of the blue luminescence of activator-free zinc sulfide.

2. Formation of Cu centers is possible in the absence of oxygen.

3. Zinc sulfide can be obtained in a state such that it does not give any inherent (blue) luminescence but is able to bring copper into a state of luminescence.

4. Oxygen can, in addition, participate in reactions associated with the action of fluxes, and it can enter into the luminophor as a component amenable to analytical determination.

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INVESTIGATION OF THE DISTRIBUTION OF COBALT THIOCYANATES BETWEEN TWO IMMISCIBLE SOLVENTS BY THE METHOD OF RADIOACTIVE INDICATORS

L.B. Levashova, E.P. Darienko and V.F. Degtyarev*

The main problems of the theory of extraction of complex compounds have hitherto not been at all fully elucidated [1, 2], and very little attention has been paid in particular to the problem of distribution of a radioactive microcomponent between two immiscible liquid phases in presence of one complex-forming compound or another [3-6]. A short survey of studies on the application of extraction to the separation of microcomponents in radiochemistry is given in the monograph of E. Broda [7].

In this work we set out to determine the coefficient of distribution and to clarify the influence of the external conditions on the process of extraction of thiocyanate complexes of cobalt. We studied the influence of the concentration of cobalt, of the concentration of thiocyanate ion, of the thermal conditions during extraction, and of the nature of the solvent.

We worked with cobalt-60 isotope as the radioactive indicator in order to have an objective method of quantitative determination of the concentration of cobalt, both in the aqueous phase and in non-aqueous phases.

EXPERIMENTAL

The principal solution used was a normal solution of $Co(NO_3)_2$ labeled with radioactive cobalt-60 isotope (half-life period 5.3 years) so that the specific activity of the original solution was 28 microcuries per 1 ml. With this specific activity, under our selected geometrical conditions of measurement, 2.5×10^5 impulses per minute per ml were obtained with a counter of the B-2M type (allowance being made for "dead" time).

At the same time an 8 N solution of ammonium thiocyanate was prepared and diluted to give 4 N and 2 N solutions.

The selected organic solvent was butyl acetate which was further purified by distillation; the 121-123° fraction was collected. Other solvents were also used: isoamyl alcohol, diethyl ether, a mixture of these in 3:1 ratio, a 1:1 mixture of isoamyl alcohol and butyl acetate.

Procedure

In order to minimize the effect of the mutual solubility of both phases in presence of ammonium thiocyanate on the magnitude of the distribution coefficient of cobalt thiocyanates, each of the selected organic solvents was divided before use into portions and previously saturated at the given temperature with an 8 N, 4 N and 2 N solution of ammonium thiocyanate. Each of these solutions in turn was saturated with the given organic solvent. Several series of experiments were run, each of which comprised the determination of the distribution coefficient of cobalt thiocyanate from 2, 4 and 8 N aqueous solutions of ammonium thiocyanate with the selected organic solvent in dependence upon the original concentration of the cobalt. For this purpose, into each of four measuring flasks, capacity of each 100 ml, were introduced with a pipet 1, 2, 5, and 10 ml of the original 1 N solution of cobalt nitrate. In the first case all the four flasks were filled to the mark with 8 N, in the second case with 4 N, and in the third case with 2 N solution of ammonium thiocyanate which had previously been saturated with the same organic solvent as was intended for the extraction. The solution in the flasks was thoroughly mixed; then from each flask were withdrawn two samples of 0.5 ml each, and the original activity of each solution was determined.

The so-prepared thiocyanate complexes were extracted. For this operation, 20 ml thiocyanate solution of cobalt complex and 20 ml of the appropriate organic solvent were transferred to a 50 ml separating funnel; the organic solvent had previously been saturated with an aqueous solution of ammonium thiocyanate of the appropriate concentration.

* G.A. Plotnikova took part in the investigation.

The separating funnels were closed, the taps and corks were thoroughly coated with paraffin wax, and the funnels were then placed for two hours in a thermostat whose temperature was kept constant to $\pm$ 0.1°. After an hour each funnel was removed from the thermostat, vigorously shaken for a strictly specified number of times, and then replaced in the thermostat where it was again kept for an hour before separation of the phases was effected.

With the help of a micropipet, 0.5-1.0 ml solution was taken (the actual amount depending on the activity) and placed in a special standard aluminum cell; the volume of solution was brought to 1 ml; the cell was then placed under the counter where measurement was carried out of the activity of the solution of each phase in two parallel tests, using both β-radiation and an end-on type of counter[8] and a standard counter of the B-2M type.

All the measurements in all experiments were performed with one and the same counter under identical geometrical conditions over a period that ensured the specified accuracy. In this case it was required that the relative statistical error of measurement of activity should not exceed 1%.

The duration t necessary for measurement of a preparation with the given relative error was determined by the formula:

$$t = \frac{(1 + k)(1 + 2k)}{N_0 \delta^2},$$

where k is the ratio of the velocity of counting of the background (N_φ imp./min.) to the velocity of counting of the activity of the test preparation with correction for the background (A imp./min.), δ is the assumed relative error, N_0 is the over-all velocity of count of the preparation + background ($A + N_\varphi = N_0$).

Incidentally it should be noted that the active solutions (both aqueous and non-aqueous) in the aluminum cell thoroughly wet the surface of the metal, so that during measurement of the liquid preparations we observe the phenomenon of spontaneous "creeping" of the active solution on to the external surface of the cell; this circumstance seriously affected the constancy of the geometrical factor and was responsible for the poor reproducibility of the results obtained.

This phenomenon was suppressed by applying a thin film of paraffin wax to the aluminum cell. In such cells the reproducibility of the results of measurements was entirely satisfactory.

As an illustration of the reproducibility of the results, the determination of the activity (on the basis of 1 ml) is set forth in Table 1.

TABLE 1

Concentration ($g/ml \cdot 10^{-3}$)	Normality of solution	Samples	Activity after making corrections	Percent deviation from mean value
0.95	0.01	1	2600	0.04
		2	2601	
1.9	0.02	1	5360	0.7
		2	5540	
4.8	0.05	1	12835	0.7
		2	12664	
9.5	0.1	1	24963	0.25
		2	25101	

Treatment of the experimental results involved application of the method of graphical representation of paired curves of distribution of the substances between the phases [9] (Fig. 1). The activity (concentration) of the original cobalt solution is plotted along the abscissas A_{origin} while the activity A_w in the aqueous phase after extraction (a, b, c) and the activity of the organic phase A_o (1, 2, 3) are plotted along the ordinates.

In addition, the character of the extraction process was studied by constructing logarithmic graphs of the change of the equilibrium activity of the cobalt in the organic phase versus the equilibrium activity of the cobalt in the aqueous phase. On the ordinates are plotted $\log A_o$ and on the abscissas $\log A_w$ on appropriate scales. The distribution coefficient was calculated from the ratio: $k = \frac{A_o^*}{A_b}$.

Evaluation of results

In Figs. 1 and 2 are represented graphically the dependence of the change of character of distribution of cobalt thiocyanate between an aqueous solution of ammonium thiocyanate (a, b, c) and butyl acetate (1, 2, 3) in dependence on the original concentration (activity) of the cobalt at 0° and 16° respectively.

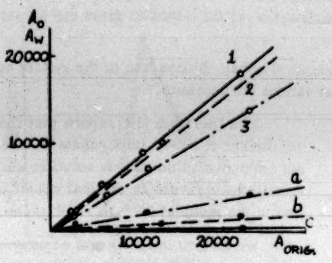

Fig. 1. Distribution of activity of cobalt thiocyanate in the system butyl acetate-aqueous solutions of ammonium thiocyanate at 0°. Explanation in text.

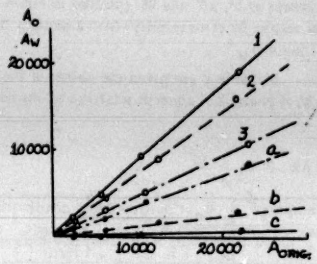

Fig. 2. Distribution of activity of cobalt thiocyanate in the system butyl acetate-aqueous solutions of ammonium thiocyanate at 16°. Explanation in text.

It is easy to see from the data that the degree of extraction of cobalt thiocyanate into the non-aqueous phase increases considerably with increase in the excess of ammonium thiocyanate and reaches its maximum value in 8 N solution.

Comparison of Figs. 1 and 2 reveals that with rising temperature the degree of extraction into the organic phase falls appreciably. This is probably due to the increase in mutual solubility of both phases and to the increased dissociation of the thiocyanate complex itself.

Extremely significant is the change in the character of the distribution of cobalt thiocyanate in the system butyl acetate-2 N aqueous solution of ammonium thiocyanate at various temperatures (Fig. 3).

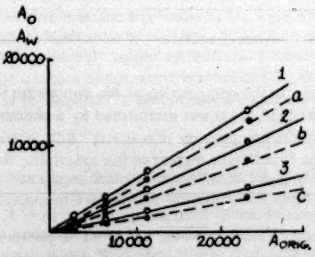

Fig. 3. Distribution of activity of cobalt thiocyanate in the system butyl acetate-2 N aqueous ammonium thiocyanate at various temperatures. 1 - 0°, 2 - 16°, a - 26°, b - 16°, c - 0°. a, b, c - aqueous phase; 1, 2, 3 - organic phase

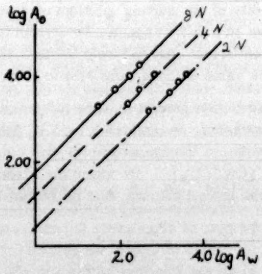

Fig. 4. Plot of the change of activity of cobalt thiocyanate between butylacetate and aqueous solutions of ammonium thiocyanate at 0°.

For the system in question at 26° the activity of the aqueous phase considerably exceeds that of the organic phase; the coefficient of distribution is $k_{o/w}$ 0.478, whereas at 0° for this system we have $k_{o/w}$ 2.75, i.e. there is reversal of the distribution between the phases.

The same experimental data were used as the basis of logarithmic plots of the change of activity of cobalt in aqueous and non-aqueous phases for the system butyl acetate-8 N, 4 N and 2 N aqueous solutions of ammonium thiocyanate at 0°, 16° and 26° (plotted in Fig. 4 for 0°). The graph shows that in each investigated system the experimental results fit satisfactorily onto a straight line whose point of intersection of the ordinates gives the numerical value of log $k_{o/w}$.

In Table 2 are given the values of the distribution coefficients of cobalt thiocyanate in the system butyl acetate-8 N, 4 N and 2 N aqueous solutions of ammonium thiocyanate at various temperatures.

TABLE 2

Temperature	Coefficients of distribution		
	Concentration of ammonium thiocyanate		
	2 N	4 N	8 N
0°	2.75	13.8	52.5
16	1.38	5.6	31.6
26	0.478	3.16	16.6

The literature [12] reports that the distribution coefficient of cobalt thiocyanate for the system aqueous ammonium thiocyanate solution-amyl alcohol remains constant for an original cobalt concentration in the range of 10^{-6} to 10^{-12} molar.

We carried out a special experiment to determine the magnitude and the character of the change of the coefficient of distribution of cobalt thiocyanate for the range of intial cobalt ion concentrations of 6 γ to 60 γ per ml.

The experiment was performed for the system butyl acetate – 2 N aqueous solution of ammonium thiocyanate solution at 16°.

The distribution coefficient ($k_{o/w}$) for this system was found to be 32.4, which is in good accord with the value obtained under the same conditions but at a starting concentration of cobalt in the range of 0.01 to 0.1 N.

It must be noted that the extraction carried out in these supplementary experiments as a rule led to a substantially colorless aqueous phase, and only the non-aqueous solutions were faintly colored. The non-aqueous phase had a deeper color after extraction of a solution containing 60 γ per ml.

Comparison of the magnitudes of the distribution coefficients of cobalt cyanates for the systems butyl acetate-2 N, 4 N and 8 N ammonium thiocyanate solutions reveals a considerable difference between them (Table 2). This deviation may be due either to the difference in ionic strength of the aqueous solutions of ammonium thiocyanate or to the varying composition of the thiocyanate complexes formed in these solutions.

The ionic strength of aqueous solutions can be increased by addition of a strong electrolyte such as an acid. Increased acidity of the starting solutions of ammonium thiocyanate led, however, not to a rise in the coefficient of distribution, but to a fall. Thus, for the system butyl acetate–2 N thiocyanate solution-hydrochloric acid at 16°, the distribution coefficient changed from 5.6 to 0.25, while for the system butyl acetate-1 N thiocyanate solution-nitric acid at 17° the value dropped from 0.14 to 0.05.

The distribution process must be influenced to a high degree by the composition of the complexes which are formed and extracted. In researches by A.K. Babko and O.F. Drako [10,11] it was established by a photometric method that ammonium thiocyanate forms with cobalt complexes of the composition $[Co(SCN)]^+$, $[Co(SCN)_2]$, $[CO(SCN)_3]^-$, $[Co(SCN)_4]^{--}$, for which the absorption maxima lie in different regions of the spectrum; for the first 530 mμ, for the second 470 mμ, and for the third and fourth 620 mμ.

For the purpose of elucidating the character of the complexes of cobalt thiocyanate formed in 8, 4, 2 and 1 N ammonium thiocyanate solutions, we carried out photometric measurements with the aid of an RF photometer of the Pulfrich type on all the solutions before and after extraction, both in aqueous and ester (butyl acetate) phases. Two absorption maxima are characteristic for various concentrations of ammonium thiocyanate in aqueous solutions before extraction and in the aqueous phases after extraction: 530 mμ and 620 mμ (Figs. 5 and 6), thus indicating the presence of the following cobalt complexes: $[Co(SCN)]^+$ $[Co(SCN)_3]^-$ $[Co(SCN)_4]^{--}$.

Only one clearly marked maximum (at 620 mμ) is observed in the ester phase under all conditions.

Consequently we can assume that butyl acetate preferentially extracts the complexes with the compositions $[Co(SCN)_4]^{--}$ and $[Co(SCN)_3]^-$.

This assumption is confirmed by a comparison of the absorption curves plotted for identical aqueous solutions before and after extraction (Figs. 5 and 6).

Thus, for 1 N solution before extraction (Fig. 5, curve 1) two maxima were found: one very conspicuous maximum at 530 mμ and one less pronounced at 620 mμ.

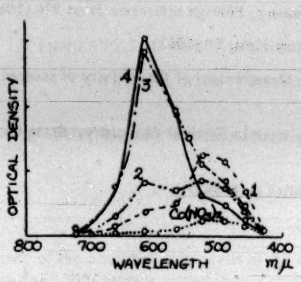

Fig. 5. Optical density of aqueous solutions of cobalt thiocyanate before extraction. Concentration of cobalt thiocyanate: 1) 1 N, 2) 2 N., 3) 4 N., 4) 8 N.

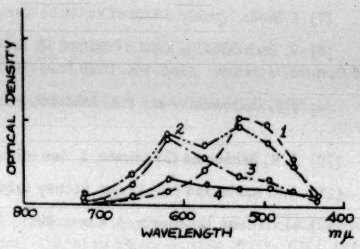

Fig. 6. Optical density of aqueous solutions of cobalt thiocyanate after extraction. Concentration of cobalt thiocyanate: 1) 1 N., 2) 2 N., 3) 4 N., 4) 8 N.

After extraction (Fig. 6, curve 1) one absorption maximum remains in the aqueous phase, corresponding to the $[Co(SCN)]^+$ complex, the value of the absorption maximum changing to an insignificant extent.

The distribution coefficient is very small (0.14) because the amount of complex extracted is small.

For 2 N ammonium thiocyanate solution the formation of both complexes is evidently equally probable, and an equilibrium is set up between them, since there is no difference in the shape of the absorption curve before and after extraction (Fig. 5 and 6, curve 2) and it has two absorption maxima at 520 and 620 mμ. This system has a small distribution coefficient (Table 2) because the solution contains two complexes, while one is preferentially extracted.

In 8 N ammonium thiocyanate solution only one absorption maximum is observed; at 620 mμ; we may consequently infer that the coefficient of distribution of cobalt thiocyanate between butyl acetate and aqueous solutions obtained in this investigation must relate to cobalt complexes with the composition $[Co(SCN)_4]^{--}$ and $[Co(SCN)_3]^-$.

We also made an experimental study of the coefficients of distribution between aqueous solutions of ammonium thiocyanate and other organic solvents (isoamyl alcohol, diethyl ether and their mixtures). It was established that these solvents are considerably poorer extractants of cobalt thiocyanate. Cobalt thiocyanate is better extracted by 1:1 mixtures of butyl acetate and isoamyl alcohol and 3:1 mixtures of isoamyl alcohol and diethyl ether. Mixtures of solvents, however, are not superior to butyl acetate in extractive power.

SUMMARY

1. It was shown that the character of the distribution of cobalt thiocyanate between butyl acetate and 8, 4, 2 and 1 N solutions of ammonium thiocyanate changes with the temperature and with the concentration of cobalt.

2. It was shown that the obtained distribution coefficients must relate to thiocyanate complexes of cobalt with the composition $[Co(SCN)_4]^{--}$ and $[Co(SCN)_3]^-$, possessing an absorption maximum at 620 mμ.

3. It was shown that the distribution of the thiocyanate complex of cobalt changes with the temperature, with the concentration of ammonium thiocyanate, and with presence of acid, but that it does not vary with change of the cobalt concentration.

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Ural Polytechnic Institute

* T.p. = C.B. Translation pagination.

INVESTIGATION OF THE INTERACTION OF THE CHLORIDES OF THE ALKALI AND THE ALKALINE EARTH ELEMENTS IN MELTS

II. THE TERNARY SYSTEM SODIUM CHLORIDE – CESIUM CHLORIDE – CALCIUM CHLORIDE

V.E. Plyushchev, I.V. Shakhno and S.A. Pozhitkova

A study of the equilibrium in melts of the chlorides of sodium, cesium and calcium is the subject of the present communication. This ternary system is here studied for the first time. One of its binary systems, NaCl – CsCl, has been studied by S. Zhemchuzhny and F. Rambakh [1]; it belongs to the simple eutectic type with polymorphic transformation of CsCl (at 451°) below the eutectic temperature. The eutectic point corresponds to 34.5 mole-% NaCl and 493°. Solid solutions are not present in the system.

The system NaCl – $CaCl_2$ was first studied by Menge [2] who reported the existence of a compound 4NaCl · $CaCl_2$ melting with decomposition at 605° and a eutectic point corresponding to 32 wt.-% NaCl and 500°. Later investigations [3] showed that this system is of the simple eutectic type; according to A.M. Pichugin [4] the eutectic point corresponds to 52.9 mole-% $CaCl_2$ and m.p. 494°. The system CsCl – $CaCl_2$ was first investigated by E.P. Dergunov and A.G. Bergman [5] in the liquidus region. The authors report the existence of a chemical compound $CsCaCl_3$. It has a singular maximum and m.p. 1030°. The chemical compound forms two eutectics with the original components of the system; the eutectic with $CaCl_2$ melts at 708°, that with CsCl at 610°. A study of the cuts of the ternary system, starting from the system CsCl – $CaCl_2$ showed inconsistency between the experimental results and the literature data on the binary system. A fresh examination was therefore undertaken of the system CsCl – $CaCl_2$, and it was established that the chemical compound CsCaCl melts without decomposition at 910°, the eutectic of $CsCaCl_3$ with CsCl (89 mole-% CsCl) melts at 612°, and the eutectic of $CsCaCl_3$ with $CaCl_2$ (89 mole-% $CaCl_2$) melts at 705°.

EXPERIMENTAL

The system NaCl – CsCl – $CaCl_2$ was studied by the visual-polythermic method. The starting sodium chloride was a chemically pure grade and was subjected to three recrystallizations.

The calcium chloride was prepared from its chemically pure hexahydrate which was dehydrated by heating and melting with continuous passage of a stream of dry hydrogen chloride to suppress appreciable formation of oxide. The oxide content of the anhydrous calcium chloride was less than 0.06%. The cesium chloride was found by spectroscopic examination to contain the following amounts of impurities (%): potassium 0.0025, sodium 0.0025, calcium 0.0018, rubidium 0.02. Salt of this purity could be used directly.

The weighed amounts of the pure chlorides were calculated from the formulas for conversion from the given composition in molar percentages to the composition in weight percentages. The method of additions of weighed amounts of sodium chloride and cesium chloride to a melt of calcium chloride or to a melt of intermediate composition enabled avoidance of the difficulty caused by the hygroscopicity of calcium chloride and led to more reliable results.

Ten sections were studied; the scheme of these is detailed in the diagram of the isotherms of the liquidus surface (Fig. 3). All the sections start from the apices of the concentration triangle. Each of the sections was regarded as a binary system in which the one component was metallic chloride and the other a mixture of two other chlorides whose ratio corresponded to the point of emergence of the section onto the formed binary system (on the opposite side).

The fusibility curves of the sections of the ternary system are represented in Fig. 1 and 2, and the corresponding experimental data are set forth in Tables 1 to 5. The compositions corresponding to points of the sections are given throughout in molar percentages. The values in parantheses were found graphically.

SUMMARY

1. A study was made by the visual-polythermic method of the interaction of the chlorides of sodium, cesium and calcium in a melt.

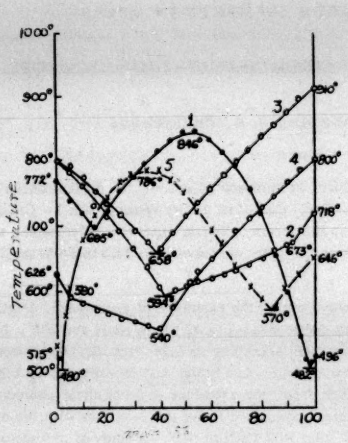

Fig. 1. Fusibility curves of sections of the ternary system.
1 - $CaCl_2 \rightarrow 35\%$ NaCl + 65% CsCl, 2 - NaCl → → 10% CsCl + 90% $CaCl_2$, 3 - NaCl → 50% CsCl + + 50% $CaCl_2$, 4 - 90% CsCl + 10% $CaCl_2$ → NaCl, 5 - 47% NaCl + 53% $CaCl_2$ → CsCl.

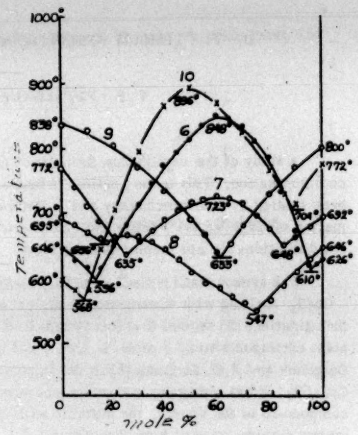

Fig. 2. Fusibility curves of sections of the ternary system.
6 - CsCl → 30% NaCl + 70% $CaCl_2$, 7 - $CaCl_2$ → 70% NaCl + 30% CsCl, 8 - 75% NaCl + + % $CaCl_2$ → CsCl, 9 - 30% CsCl + 70% $CaCl_2$ → → NaCl, 10 - 10% NaCl + 90% CsCl → $CaCl_2$.

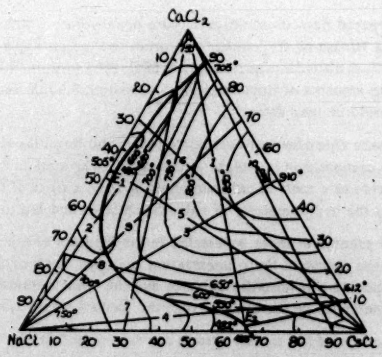

Fig. 3. Surface of crystallization of the system NaCl– CsCl – $CaCl_2$ with the scheme of the sections through the system.

TABLE 1

Sections 1 and 2 of the system $NaCl - CsCl - CaCl_2$

Section 1		Section 2	
$CaCl_2 \rightarrow$ {35% NaCl, 65% CsCl}		$NaCl \rightarrow$ {10% CsCl, 90% $CaCl_2$}	
$CaCl_2$ (mole-%)	Temperature	NaCl (mole-%)	Temperature
100.0	772°	100.0	800°
95.0	740	95.0	785
90.0	727	90.0	763
85.0	695	85.0	731
80.0	724	80.0	714
75.0	752	75.0	691
70.0	777	70.0	667
65.0	796	65.0	637
60.0	814	60.0	604
55.0	832	(58.5)	(594)
50.0	844	55.0	597
(47.5)	(846)	50.0	606
45.0	844	45.0	611
40.0	832	40.0	619
35.0	813	35.0	624
30.0	790	30.0	631
25.0	755	25.0	639
20.0	718	20.0	648
15.0	654	15.0	657
10.0	596	10.0	669
5.0	528	7.8	673
2.0	492	5.0	693
(1.3)	(482)	0.0	718
1.0	487		
0.0	496		

TABLE 2

Sections 3 and 4 of the system $NaCl - CsCl - CaCl_2$

Section 3		Section 4	
$NaCl \rightarrow$ {50% CsCl, 50% $CaCl_2$}		$NaCl \rightarrow$ {90% CsCl, 10% $CaCl_2$}	
NaCl (mole-%)	Temperature	NaCl (mole-%)	Temperature
100.0	800°	100.0	800°
95.0	792	95.0	783
90.0	774	90.0	764
85.0	755	85.0	742
80.0	735	80.0	724
75.0	718	75.0	708
70.0	694	70.0	690
65.0	674	65.0	668
(61.5)	(658)	60.0	648
60.0	665	55.0	627
55.0	688	50.0	604
50.0	712	45.0	574
45.0	735	40.0	540

TABLE 3

Sections 5 and 6 of the system $NaCl - CsCl - CaCl_2$

Section 5		Section 6	
$CsCl \rightarrow$ {47% NaCl, 53% $CaCl_2$}		$CsCl \rightarrow$ {30% NaCl, 70% $CaCl_2$}	
CsCl (mole-%)	Temperature	CsCl (mole-%)	Temperature
100.0	646°	100.0	646°
95.0	626	95.0	631
90.0	598	90.0	615
85.0	575	(86.8)	(596)
(84)	(570)	85.0	614
80.0	586	80.0	647
75.0	606	75.0	680
70.0	630	70.0	712
65.0	668	65.0	743
60.0	694	60.0	771
55.0	720	55.0	792
50.0	753	50.0	812
45.0	774	45.0	834
40.0	783	40.0	848
35.0	786	35.0	842
30.0	780	30.0	827
25.0	766	25.0	807
20.0	743	20.0	783
15.0	715	15.0	733
10.0	678	10.0	665
5.0	600	5.0	618
3.0	566	(4)	(610)
(1.7)	(480)	2.0	620
1.0	498	0.0	626
0.0	515		

TABLE 4

Sections 7 and 8 of the system $NaCl - CsCl - CaCl_2$

Section 7		Section 8	
$CaCl_2 \rightarrow$ {70% NaCl, 30% CsCl}		$CsCl \rightarrow$ {75% NaCl, 25% $CaCl_2$}	
$CaCl_2$ (mole-%)	Temperature	CsCl (mole-%)	Temperature
100.0	772°	100.0	646°
95.0	740	95.0	626
90.0	710	90.0	606
85.0	691	85.0	586
80.0	655	80.0	566
75.0	635	75.0	547
70.0	655	70.0	559
65.0	672	65.0	571
60.0	687	60.0	582
55.0	702	55.0	593
50.0	715	50.0	607
45.0	720	45.0	625
40.0	723	40.0	644

(continued on next page)

TABLE 2 (Continued)

Section 3		Section 4	
NaCl → 50% CsCl, 50% $CaCl_2$		NaCl → 90% CsCl, 10% $CaCl_2$	
NaCl (mole-%)	Temperature	NaCl (mole-%)	Temperature
40.0	754	35.0	545
35.0	774	30.0	551
30.0	795	25.0	557
25.0	815	20.0	563
20.0	835	15.0	572
15.0	854	10.0	580
10.0	875	5.0	590
5.0	895	0.0	626
0.0	910		

TABLE 4 (Continued)

Section 7		Section 8	
$CaCl_2$ → 70% NaCl, 30% CsCl		CsCl → 75% NaCl, 25% $CaCl_2$	
$CaCl_2$ (mole-%)	Temperature	CsCl (mole-%)	Temperature
35.0	720	35.0	656
30.0	714	30.0	662
25.0	697	25.0	664
20.0	675	20.0	662
15.0	648	(17.3)	(656)
10.0	660	15.0	660
5.0	675	10.0	670
0.0	692	5.0	680
		0.0	695

TABLE 5

Sections 9 and 10 of the system NaCl – CsCl – $CaCl_2$

Section 9		Section 10	
NaCl → 30% CsCl, 70% $CaCl_2$		$CaCl_2$ → 10% NaCl, 90% CsCl	
NaCl (mole-%)	Temperature	$CaCl_2$ (mole-%)	Temperature
100.0	800°	100.0	772°
90.0	768	90.0	712
80.0	726	(88)	(704)
70.0	680	85.0	727
65.0	654	80.0	764
(61.3)	(633)	70.0	822
60.0	638	60.0	866
55.0	662	50.0	896
50.0	690	40.0	862
40.0	735	30.0	795
30.0	772	20.0	706
20.0	804	15.0	643
10.0	825	10.0	581
0.0	838	(8.6)	(568)
		5.0	580
		0.0	600

2. The isotherms of the liquidus surface of the system sodium chloride – cesium chloride – calcium chloride were plotted.

3. Four fields of primary crystallization were detected in the system: NaCl, CsCl, $CaCl_2$, and $CsCaCl_3$.

4. Two ternary eutectics crystallize at 480° (E_1) and 482° (E_2); the corresponding compositions are: E_1 – NaCl 46.2 mol.-%, CsCl 1.7 mol.-% and $CaCl_2$ 52.1 mol.-%; E_2 – NaCl 34.5 mol.-%, CsCl 64.2 mol.-% and $CaCl_2$ 1.3 mol.-%.

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Moscow Institute of Fine Chemical Technology

SOLUBILITY OF CALCIUM SULFATE IN SOLUTIONS OF HYDROCHLORIC ACID AT 25°

I.G. Ryss and E.L. Nilus

The sulfate ion is a common impurity in commercial hydrochloric acid produced by the sulfate process. The present All-Union Standard specifies a content of SO_4'' in liquid zinc chloride (not more than 0.5% SO_4'' with 20.0% Zn) such that the employment of commercial hydrochloric acid of second quality (GOST 1382-42; up to 0.6% SO_3 with 27.5% HCl) cannot lead to formation of standard "liquid" zinc chloride even when there is no loss of HCl by evaporation and there are no other sources of contamination of the solution of zinc chloride by sulfate ion.

In such cases it is usual to resort to precipitation of the sulfate in the zinc chloride solution by the action of calcium chloride; part of the product is then lost, however, in the voluminous precipitate of calcium sulfate. For this reason it was of interest to examine the possibility of lowering the content of SO_3 in hydrochloric acid.

The application of barium chloride for precipitation of SO_4'' is inexpedient due to the high cost; this process is also slow, since $BaCl_2$ is very poorly soluble in hydrochloric acid solutions and the reaction is heterogeneous.

An objection to the use of calcium chloride would appear to be the considerable rise in solubility of calcium sulfate in presence of hydrochloric acid. According to the literature [1] the solubility of $CaSO_4 \cdot 2H_2O$ at 25° in hydrochloric acid continuously rises throughout the whole region of investigated concentrations of HCl (up to 7%). The rise of solubility of $CaSO_4 \cdot 2H_2O$ in hydrochloric acid is the normal consequence of the effect of the "foreign-ion" electrolyte – fall in the activity coefficient of ions of Ca'' and SO_4'' with the rise of ionic strength of the solution.

A number of instances are known in which the activity coefficients pass through a minimum and start to rise with further increase of the water concentration. From the standpoint of the hydrate theory of Mendeleev, this phenomenon is due to binding of a considerable portion of the water in the solution to the relatively stable hydrates. For example, $CaSO_4 \cdot 2H_2O$ behaves in this manner in solutions of CrO_3[2] and phosphoric acid [3]. In 1942 I.G. Ryss also confirmed it for the case of solubility of gypsum in hydrochloric acid, and at one of the factories the purification of acid from SO_4'' by introduction of calcium chloride was put into practice.

Data was later published by A.M. Kuznetsov [4] for the solubility of "anhydrous $CaSO_4$" in hydrochloric acid at 20°. The author kept the salt in contact with the acid for 10 days (occurrence of mixing was not mentioned). The composition of the solid phase at the close of the experiment was not determined. The solutions formed had the following compositions:

% HCl before saturation	4.0	8.0	13.0	16.0	20.0
Content of $CaSO_4$ in g 1000 g initial acid	15.75	19.80	18.78	16.11	12.64

In the present work a study was made of the solubility of calcium sulfate at 25° in a wide range of HCl concentrations, and of the conditions of precipitation of calcium sulfate from the solutions.

EXPERIMENTAL

1. Solubility of calcium sulfate in hydrochloric acid at 25°. $CaSO_4 \cdot 2H_2O$ was prepared by the action of 10% chem. pure sulfuric acid on a 1 M solution of chem. pure calcium chloride, and washing the precipitate with water, alcohol and ether. The product did not contain qualitatively detectable amounts of H^+ and Cl^-. The purity of the substance was confirmed by determination of the water content (2.005 moles water per mole $CaSO_4$) and of the optical constants.

Experimental procedure. Tightly closed test tubes containing hydrochloric acid solution and excess of precipitated gypsum were shaken for a week at room temperature (25-28°). The test tubes were then inverted for 8 hours in a thermostat at 25.00 ± 0.05°. Part of the solution was drawn off at the same temperature. Analyses were performed on the solutions and on the wet precipitates (in order to establish the composition of the solid phase by the method of residues).

Analytical procedure. The HCl content was determined by titration with caustic alkali;* The $CaSO_4$ content was determined by evaporation in presence of a very slight excess of sulfuric acid, by calcination at 600-700°, and by weighing. Tests showed this method to be perfectly accurate.

Experimental results. The results of determination of the solubility of $CaSO_4 \cdot 2H_2O$ in solutions of hydrochloric acid at 25° are set forth in Table 1. The composition of the liquid phase is the mean of two determinations; individual determinations did not vary by more than ± 0.01% $CaSO_4$ and ± 0.02% HCl. Only in the case of approx. 30.6% HCl solution did the variation in the acidity of parallel runs differ by as much as ± 0.5%; evidently in this case a part was played by evaporation of hydrogen chloride during separation of the precipitate and taking of the sample. In experiments 3, 6, 7, 8 and 10 the $CaSO_4$ content of the solution was determined on one sample.

TABLE 1

Experiment No.	Composition of liquid phase (in wt.-%)		Composition of moist precipitate (in wt.-%)		Bottom phase
	HCl	$CaSO_4$	HCl	$CaSO_4$	
1	3.56	1.50	2.48	25.02	$CaSO_4 \cdot 2H_2O$
2	6.48	1.80	2.43	52.05	
3	9.15	1.85	4.61	40.22	
4	12.08	1.73	4.69	51.19	
5	15.09	1.56	2.73	66.81	
6	18.33	1.27	12.67	25.60	
7	21.15	1.04	7.35	52.44	
8	24.26	0.88	9.94	47.01	
9	26.73	0.75	6.08	61.83	
10	30.61	0.64	16.33	46.78	$CaSO_4$ (anhydrite)

As shown by Fig. 1, the data of [1] in the investigated region are somewhat below our values. The solubility of gypsum reaches a maximum at an HCl concentration of about 9%. The bottom phase in experiments 1-9 was gypsum; in 10 it was anhydrite; the solubility of anhydrite deviates to an insignificant extent from the course of gypsum solubility curve. This is because, first, the experimental point lies close to the gypsum ⇌ anhydrite transformation point, and second, the solubility branches of gypsum and anhydrite are bound to intersect at an extremely small angle.

It can be thermodynamically calculated [5] that the activity of saturated solutions of gypsum (a') and anhydrite (a) are related by the expression

$$\frac{a}{a'} = \left(\frac{p_{sat}}{p}\right)^2,$$

where $p_{sat.}$ is the pressure of the water vapor of the solution and p is the pressure of dissociation of gypsum to anhydrite.

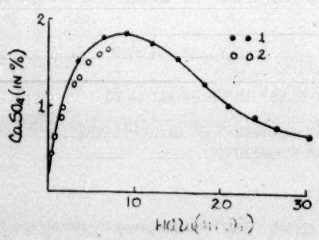

Fig. 1. Solubility of calcium sulfate in hydrochloric acid at 25°.
1 - Our data; 2 - data in [1].

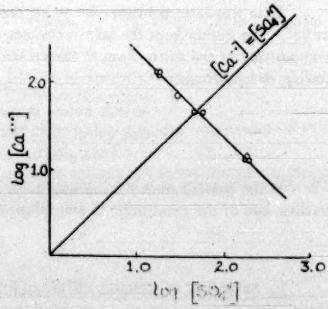

Fig. 2. Influence of excess of Ca^{++} and SO_4^{--} on the solubility of $CaSO_4 \cdot 2H_2O$ in 28% HCl at 25°.

In the vicinity of the transformation point, $p_{sat.}/p$ is close to unity, and since this fraction is raised to a small power, a and a' differ only very slightly from each other. The activity coefficients of the dissolved substances in the main are governed by the concentration of hydrochloric acid, and for gypsum and anhydrite they substantially coincide; hence the solubilities must also be similar. A similar insignificant difference between the solubility curves

* A weighed amount of mother liquor was made up to 100 ml in a measuring flask; 25 ml portions of the sample were titrated.

of anhydrite and gypsum close to the transition point was observed by A.A. Taperova and M. N. Shulgina [5] in phosphoric acid solutions.

The samples of experiments 8 and 8 correspond to metastable equilibrium. Actually, complete transformation of gypsum into anhydrite was detected under the microscope, a year after carrying out of the main experiments in the samples from experiments 8 and 9 which had been stored at room temperature. In other samples the bottom phase was still gypsum. After continued storage for another half year at 12-18°, no further change of composition of the bottom phase had taken place. In particular, not a single crystal of gypsum was detected in samples 8 and 9. There is no doubt that the stable phase at 25° is gypsum when the HCl concentration is 21.15% and lower.

Interpolation of van't Hoff's measurements [6] of the pressure of dissociation of gypsum to anhydrite leads to a value for p_{H_2O} of 15.3 mm at 25°.*

According to data of [7], this pressure of water vapor over hydrochloric acid at 25° is reached at a concentration of about 18.2% HCl. The water vapor pressure over 22% hydrochloric acid is equal to 12.6 mm. Consequently, either the values for the dissociation pressure of gypsum are too high or the data for the pressure of water vapor over hydrochloric acid solutions are too low.

It could be suggested that when the HCl concentration (which in the main determines the ionic strength of the solution) is constant, the activity coefficients of the $Ca^{\cdot\cdot}$ and $SO_4^{\cdot\cdot}$ ions are approximately constant. In this case the solubility product $L' = [CA^{\cdot\cdot}][SO_4^{\cdot\cdot}]$ ** should also be constant, although its absolute value must differ appreciably from the value of the solubility product in dilute aqueous solutions. A similar relation was previously observed by one of us [2] for the solubility of calcium chromate in presence of excess of $Ca^{\cdot\cdot}$ and $CrO_4^{\cdot\cdot}$.

Results of measurements of the solubility of gypsum in mixtures of HCl and $CaCl_2$ and in mixtures of HCl and H_2SO_4 at 25° are set forth in Table 2. They confirm the applicability of this relation also to the present case. In experiments with excess of $Ca^{\cdot\cdot}$, the $SO_4^{\cdot\cdot}$ content was determined by precipitation as $BaSO_4$ after previous removal by evaporation of a considerable part of the HCl.

The product $[CA^{\cdot\cdot}][SO_4^{\cdot\cdot}]$ also satisfactorily agrees with the data of Table 1 calculated by interpolation. Similar values of the solubility product were also obtained in the experiment on gypsum precipitation described below. All these data are graphically represented in Fig. 2. The very slight deviation of points from the straight line at an angle of 135° is associated with variations in the HCl concentration.

TABLE 2

Expt. No.	HCl (wt.-%)	Concentration $Ca^{\cdot\cdot}$	Concentration $SO_4^{\cdot\cdot}$	$[CA^{\cdot\cdot}][SO_4^{\cdot\cdot}]$	Bottom phase
		mg-ions / 1000 g solution			
1	27.96	135.4	18.16	2459	$CaSO_4 \cdot 2H_2O$
2	27.72	135.8	18.19	2470	
3	28.45	13.68	181.4	2482	
4	28.43	13.77	182.7	25.16	

2. Precipitation of $CaSO_4$ from hydrochloric acid. For evaluation of the role of supersaturation in the precipitation of gypsum the following experiment was carried out: To samples of hydrochloric acid containing some $SO_4^{\cdot\cdot}$ was added calcium chloride, and the mother liquors were analyzed immediately after mixing, after 4 hours, and after standing for a week followed by 8-hours' stirring in a thermostat. ***

Gypsum and individual crystals of anhydrite were detected under the microscope in all samples. Results of analyses are set forth in Table 3.

Thus, after 4 hours the supersaturation of the solution remained extremely slight, and keeping for this period proved adequate in practice. The values of L for 28.68% HCl are just a little low (they correspond to a drop of 0.03% in the solubility of $CaSO_4$ in comparison with the values given above).

3. Calculation of the proportion of calcium chloride. Since the solubility of calcium sulfate in concentrated hydrochloric acid increases sharply with rising temperature and also increases with falling concentration of hydrochloric acid, it is logical to conduct the purification at room temperature or at a lower temperature in acid of the highest possible concentration.

* We take the opportunity of pointing out that the data in the tenth volume of the "Handbook of physical, chemical and technological constants" of the Technical Encyclopedia on the heats of dehydration of gypsum are erroneous; they correspond to the formation of liquid water and not of water vapor.

** For simplification, the concentrations are expressed in mg-ions/1000 g solution.

*** The latter data correspond to the equilibrium of the solubility of gypsum.

TABLE 3

Concentrations of $[Ca^{\cdot\cdot}]$ and $[SO_4^{\cdot\cdot}]$ (in mg-ions/1000 g solution) and solubility product

Time of determination	Concentration of HCl (in weight-%)											
	28.88			27.87			28.17			28.68		
	$[Ca^{\cdot\cdot}]$	$[SO_4^{\cdot\cdot}]$	L'	$[Ca^{\cdot\cdot}]$	$[SO_4^{\cdot\cdot}]$	L'	$[Ca^{\cdot\cdot}]$	$[SO_4^{\cdot\cdot}]$	L'	$[Ca^{\cdot\cdot}]$	$[SO_4^{\cdot\cdot}]$	L'
Immediately after mixing	14.37	199.5	2870	49.65	61.18	3040	137.2	22.41	3100	83.43	40.84	3400
After 4 hours	12.80	196.0	2510	45.90	57.74	2640	132.7	18.01	2390	72.73	31.65	2310
After 7 days	12.78	195.7	2500	45.26	57.18	2590	-	17.01	-	72.33	30.78	2230

For avoidance of supersaturation, the calcium chloride should be introduced not later than 4-5 hours before utilization of the acid at 25° or 6-8 hours at 0°.

The proportion of $CaCl_2$ to be added may be calculated as follows: If the $SO_4^{\cdot\cdot}$ content of the acid has to be lowered from A% to B%, then to each 100 kg acid must be added $\frac{40}{96}(A-B)$ kg calcium ions to bind the $SO_4^{\cdot\cdot}$ as a precipitate. Furthermore, the $Ca^{\cdot\cdot}$ concentration in the acid must be equal to K/B, where K is the solubility product expressed in percentages of $Ca^{\cdot\cdot}$ and $SO_4^{\cdot\cdot}$. *

Neglecting, for the sake of simplification, the change of weight of the acid due to introduction of $CaCl_2$ and separation of the precipitate, we find the total consumption of calcium ions in kg per 100 kg acid:

$$Z = 0.416\,(A-B) + \frac{K}{B} = 0.416\,(A-B) + \frac{3.84 \cdot 10^{-5} \cdot L'}{B}$$

The values of K can be calculated on the basis of the data set forth above. For example, for 28% HCl at 25°, L' = 2640 and K ≅ 0.101.

For calculation of the conditions of purification of hydrochloric acid at other temperatures, we can apply similar formulas, using our determined values of K = %Ca·%SO_4 in 28% hydrochloric acid:

Temperature	0°	16°	50°
K	0.046	0.06	0.35

SUMMARY

1. The solubility of gypsum in hydrochloric acid at 25° reaches a maximum at an HCl concentration of about 9%.

2. Gypsum remains the stable bottom phase in solutions containing up to 21.15% HCl. At concentrations of HCl up to 27%, the transition of gypsum to anhydrite proceeds extremely slowly; in 30.61% HCl the transition is rapid.

3. At constant HCl concentration the solubility product of $Ca^{\cdot\cdot}$ and $SO_4^{\cdot\cdot}$ ions remains constant.

4. A method is given for calculating the amount of calcium chloride to be added to purify the acid from $SO_4^{\cdot\cdot}$.

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Dniepropetrovsk Institute of Metallurgy

* Since $[Ca^{\cdot\cdot}] = \%\,Ca^{\cdot\cdot} \cdot \frac{10000}{40}$ and $[SO_4^{\cdot\cdot}] = \%\,SO_4^{\cdot\cdot}\,\frac{10000}{96}$, to $K = \%Ca^{\cdot\cdot} \cdot \%\,SO_4^{\cdot\cdot} = 3.84 \cdot 10^{-5} \cdot L'$.

DIAGRAM OF THE PHASE TRANSFORMATIONS OF THE SYSTEM $H_2O - NH_3$

K. E. Mironov

As far back as 1869 D.I. Mendeleev, in a consideration of the properties of ammonium and of the behavior of aqueous solutions of ammonia, arrived at the conclusion that ammonium hydroxide, "an unstable substance, which decomposes" [1], can exist at low temperatures. He then went on to make the more definite statement: "possibly with intense cooling ammonium hydroxide NH_4OH can be obtained in the solid state" [2]. Subsequent investigations of the liquidus of the system $H_2O - NH_3$ unequivocally established the existence of two hydrates of ammonia: $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$, which melt without decomposition at about −79° [3-8].

It has also been suggested that a continuous series of mixed crystal (solid solutions) is formed in the system $H_2O - NH_3$ [9]; this claim has not been refuted. Elliott [8] attempted to demonstrate the non-existence of solid solutions by visual observation of the appearance of a mixture of crystals of different forms, but evidently what he had in mind was a mechanical mixture of the two crystalline phases. Isolated determinations of the temperatures of the solidus [7,8] do not prove the absence of solid solutions in the system $H_2O - NH_3$. The purpose of the present investigation was to resolve the problem of the existence of solid solutions in the system $H_2O - NH_3$ by the method of thermal analysis which had fully justified itself in the investigation of the system $H_2O - H_2O_2$ [10].

EXPERIMENTAL

Experimental method. The temperature of the liquidus was determined by the visual-polythermal method, slightly modified for working in the region of low temperatures [11]; the temperature of the solidus was established by visual observation of the cooling and heating curves, readings being taken every 10 seconds. The compositions were cooled in a Dewar flask over liquid nitrogen. The temperature was measured with a nichrome-constantan thermocouple calibrated from the melting points of water 0°, mercury −38.9° [12], acetone −94.2°, and diethyl ether (−116.3° for the α-modification and −123.3° for the β-modification [13]). Temperatures were recorded by means of a microameter with a shaded pointer (M-91 type) with a scale 150 mm long; this permitted measurement of temperatures to 0.2° at a recording accuracy of 0.2 mm.

Change of concentration of the compositions was affected by additions of water. In order to preclude volatilization of ammonia, the additions were made with a long pipet through a special glass tube in a rubber stopper, directly at the surface of the frozen compositions cooled to about 120°. After introduction of the addition, the glass was tightly closed and the resultant new composition was slowly melted while stirring with a stirrer fitted with a mercury seal.* After addition of 1.138 g H_2O to 1.414 g NH_3 weighed in a test tube under a tightly fitting rubber stopper with a special grip of steel wire, a further 12 additions of water were made to the obtained solution and the solution contained (by calculation) 20.6% NH_3 (all percentages are by weight). Titration of a weighed sample with 0.1 N H_2SO_4 using methyl red as indicator [14] gave a content of 20.35 and 20.39% NH_3, i.e. it was proved that the method of additions was applicable [15] to the study of the system $H_2O - NH_3$. Apart from the analytical control, the reliability of the results of an individual series of 10-12 additions was verified by two to three points of the succeeding series of additions.

Substances. The ammonia used was dried by condensation over metallic sodium and by passage through U-tubes containing packing covered with a layer of metallic sodium and lumps of KOH [16]. The so-purified ammonia did not leave a noticeable residue on evaporation and had m.p. −76.5°; this is higher than the handbook values [12] but corresponds to values reported in the literature [17] and is confirmed by the cooling curves (Fig. 2). The water for the experiments was distilled once.

Results of measurements. The liquidus of the system was determined from data for 56 compositions and the solidus from data for 25 compositions. Considerable supercooling was observed with compositions containing 25-70% NH_3, particularly in the 25-45% NH_3 region; for precise determination of the liquidus, we therefore introduced seed crystals prepared from the solution under examination. Determination of the solidus necessitated supplementary introduction into the incipiently crystallizing solution of a seed of the secondarily crystallizing phase. In regions of very intense supercooling, the temperatures of the solidus and liquidus were determined from the results of heating right up to disappearance of the last crystals. Results as a whole are represented in Fig. 1, and the most important of the numerical measurements are set forth in Table 1.

The line obtained for the liquidus confirms the formation of two compounds $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$, melting without decomposition at −77.0 and −77.4° respectively. Judging by the indicated limits of supercooling compositions, supercooling is most characteristic of the compound $NH_3 \cdot H_2O$.

* This enabled measurements to be made without loss of ammonia.

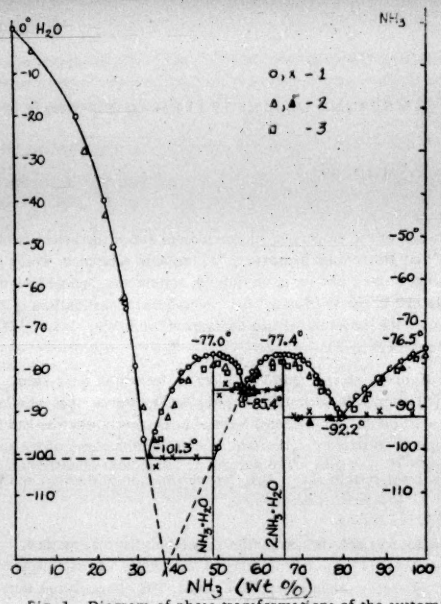

Fig. 1. Diagram of phase transformations of the system $H_2O - NH_3$.
1) liquidus, solidus from author's data; 2) the same from data in [7]; 3) liquidus from data in [8].

For solutions with a content of up to 32.7% NH_3 (region of primary separation of the ice phase) the temperature of eutectic crystallization could not be determined. The compound $NH_3 \cdot H_2O$ crystallizes in this region with very great difficulty (secondary phase). In a few cases the solid phase had increased in bulk to such an extent during crystallization of the eutectic that the test tube which had been filled with solution was broken into small pieces; consequently the solidus of the 0-32.7% NH_3 region is inserted hypothetically in the diagram.

EVALUATION OF RESULTS

Results of measurements confirm the crystallization of the monohydrate and the hemihydrate of ammonia in the system $H_2O - NH_3$ on cooling. The monohydrate of ammonia corresponds in composition to ammonium hydroxide NH_4OH, whose existence below −18° was predicted by D.I. Mendeleev. None of the authors [3-8] mentions this fact, although Mendeleev's Principles of Chemistry has been well known for a long time in other countries [18]. In justice D.I. Mendeleev deserves recognition as the first to indicate the possibility of isolation of ammonia monohydrate in the solid state. In Gmelin [19] there is a report that ammonium oxide $(NH_4)_2O$, corresponding in composition to the hemihydrate of ammonia, was prepared in 1888. This is erroneous, since Maumené [20] understood by the term "ammonia protoxide H_3NO" not ammonium oxide, but hydroxylamine NH_2OH.

Both of the compounds formed in the system melt at low temperatures, which indicates [21] the absence from them of an ionic type of bond and permits us to express their composition by the molecular formulas $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$. These compounds are formed as a result of hydrogen bonding [22].

The melting points found for these compounds are approximately 2° higher than those found by other authors; the temperatures of the eutectics in the main are the same (Table 2).

Visual observations, confirmed by the cooling and heating curves, sufficiently clearly demonstrate that the melting point of $NH_3 \cdot H_2O$ is −77.0° and that of $2NH_3 \cdot H_2O$ is −77.4° (Fig. 2). The temperatures of the liquidus, which agree with other authors' data [5, 7, 8], corresponded to abundant separation of crystals. This is evidence of supercooling of the solutions and enables us to regard the data of previous workers as a little too low.

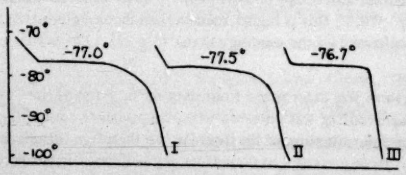

Fig. 2. Cooling curves for compounds of the system $H_2O - NH_3$.
I) $NH_3 \cdot H_2O$, II) $2NH_3 \cdot H_2O$, III) pure NH_3.

In contrast to the ineffective attempts to show the absence of mixed crystals by visual observation of crystallization above the temperature of the solidus [8], the results of the present investigation bring confirmation of the fact that solid solutions (mixed crystals) are absent from the system $NH_3 - H_2O$. This is proved for compositions with more than 32.7% NH_3 by the eutectic crystallization; for the region below 32.7% NH_3 the same conclusion can be reached from the absence of solid solutions in the ice phase [2].* For compositions intermediate between the compounds $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$, eutectic effects are obtained on the time/temperature curves, and therefore Friedrich's claim of the existence of a continuous series of mixed crystals is erroneous.

* A report of the existence of solid solutions in the ice phase for the system $H_2O - NH_4F$ [24] bears a tentative character and calls for confirmation by detailed data.

TABLE 1

Temperatures of liquidus and solidus determining the absence of solid solutions in the system $H_2O - NH_3$

Experiment No.	NH_3 in solution, (in weight-%)	Temperature: Of liquidus	Temperature: Of solidus	Crystallizing solid phases (in order of separation)
1	100	−76.5°	−76.7°	NH_3
3	96.6	−78.5	−91.6	$NH_3 + 2NH_3 \cdot H_2O$
7	85.6	−85.5	−91.0	
11	79.0	−90.3	−92.4	
15	71.8	−79.7	−90.6	$2NH_3 \cdot H_2O + NH_3$
18	68.7	−77.7	−92.1	
21	65.4	−77.3	−77.5	$2NH_3 \cdot H_2O$
22	64.9	−77.5	−85.0	$2NH_3 \cdot H_2O + NH_3 \cdot H_2O$
26	59.0	−81.3	−85.3	
29	56.3	−85.1	−85.6	$NH_3 \cdot H_2O + 2NH_3 \cdot H_2O$
	50.1	−77.0	−86.7	
36	The same	−99.0	could not be determined	$2NH_3 \cdot H_2O$ + ice (?)
38	48.6	−77.2	−77.0	$NH_3 \cdot H_2O$
41	44.5	−77.6	−101.3	$NH_3 \cdot H_2O$ + ice
46	36.1	−90.3	−101.3	
48	32.0	−96.7	could not be determined	ice + $NH_3 \cdot H_2O$
52	24.4	−51.4		
55	15.1	−20.5		
56	0.0	− 0.0	0.0	ice

TABLE 2

Invariant points of the system $H_2O - NH_3$ (composition in weight-%)

Eutectic of $NH_3 + 2NH_3 \cdot H_2O$		Eutectic of $2NH_3 \cdot H_2O$		Eutectic of $2N_3 \cdot H_2O + NH_3 \cdot H_2O$		$NH_3 \cdot H_2O$		Eutectic of $NH_3 \cdot H_2O$ + ice		Literature
Composition	Melting point	Composition	Melting point	Composition	Melting point	Composition	Melting point	Composition	Melting point	
80.3	−94.0°	65.4	−79.0°	56.5	−87.0°	48.6	−80.0°[b]	34.0°[b]	−125.0°[b]	[3]
79.8[a]	−92.6	65.4	−79.4[b]	56.7[a,b]	−87.3	48.6	−79.5[b]	34.3[a,b]	−100.9[b]	[5]
80.7[a]	−92.5	65.4	−78.8	57.2[a,b]	−86.0	48.6	−79.0	33.5[a]	−102.3	[7]
78.4[a,b]	−94.7[b]	65.4	−78.6[b]	57.7[a,b]	−88.2[b]	48.6	−79.0[b]	31.3[a,b]	−102.5[b]	[8]
79.9	−92.2	65.4	−77.4	56.7	−85.4	48.6	−77.0	32.7	−101.3	Author's data

Notes: a) Converted from mole-%. b) Data claculated from graph; no mention in text.

The compound $NH_3 \cdot H_2O$ has a greater tendency to supercool. The primary crystallization established for a composition with 50.1% NH_3 at −99°, i.e. well in the region of supercooling of $NH_3 \cdot H_2O$, may probably correspond to separation of the $2NH_3 \cdot H_2O$ phase on the metastable continuation of the branch of primary crystallization of this compound (Fig. 1, Table 1, experiment 36). Other metastable points could not be found, but some of them have probably been found by other workers [5, 8]; the possibility is therefore not excluded that a special investigation will reveal the metastable portion (broken line in Fig. 1) of the liquidus with a eutectic at −127° (extrapolated).

SUMMARY

1. The form of the fusibility diagram of the system $H_2O - NH_3$ was confirmed. The compounds formed, $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$, melt at −77.0, and −77.4° respectively, as was confirmed by the cooling curves.

2. Solid solutions are not formed in the system $H_2O - NH_3$. The temperatures of eutectic crystallization are 101.3°, −85.4° and −92.2°; the composition of the eutectic points is 32.7, 56.7 and 79.9% NH_3 respectively.

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Institute of General and Inorganic Chemistry
of the Academy of Sciences of the USSR

THE HYDROGEN BOND AND THE PHYSICAL PROPERTIES OF SOME SUBSTITUTED PHENOLS AND ANISOLES

II. HALOGEN-SUBSTITUTED PHENOLS*

A. E. Lutsky

The varying extents to which atoms tend to form inter- and intramolecular hydrogen bonds are explained on the basis of their electronegativity and size [2]. This led to the dissemination of the theory that fluorine is the only halogen that forms a stable hydrogen bond; chlorine was said to manifest this property to an extremely slight extent, while it was supposed to be entirely lacking in bromine and iodine. This theory is inconsistent, however, with the properties of the halogen-substituted phenols.

The branching and slight shift of the absorption band of the OH group in the region of the first and second harmonic band led to the suggestion that o-chlorophenol consists mainly of molecules of the cis form which is stabilized by a hydrogen bond within the molecule. The greater shift of the maximum of the band attributed to the cis form in o-bromo- and o-iodophenols presupposes not only the presence but also a greater strength of the hydrogen bond in comparison with o-chlorophenol. This bond strength falls in the order: I > Br > Cl > F [3]. In a number of cases the spectral data compel us to admit that the O–H...Br bond is even stronger than the O–H...B bond [4]. Data for the dipole moment also show the ability of all the halogens to participate in the formation of an intramolecular hydrogen bond [5]; however, the character of the change of the dipole moment of the compounds in question in dioxan implies a fall in strength of the bond in the following order (the opposite of what is inferred from spectral data): F > Cl > Br [6]. Further evidence for the formation of a hydrogen bond by all the halogens is provided by many chemical properties of halogenphenols, e.g. the stability of 3-halogenobenzoquinone-4-oximes [7], the formation of molecular compounds with cyclic oxides [8], the yield of ortho-isomer in the Reimer-Tiemann reaction [9], etc.; some of these reactions lead to the conclusion that the strength of the intramolecular bond falls in the order I > Br > Cl, others that the fall is in the order of Cl > Br > I.

Association of molecules is markedly reflected in the physical properties of macrosubstances in the liquid state [10] and of their solutions [11]. In Table 1 are set forth the values of density (d), surface tension (γ) and viscosity (η) of o- and p-chlorophenols and anisoles at 131 and 172°. Their boiling points are also given. The relative values of all these properties of the isomers of hydroxy and methoxy compounds and others confirm the opinion that o-chlorophenol contains a firm intramolecular hydrogen bond [12]. Actually its density is appreciably lower than that of its isomer (0.056 less at 131°); passage to the methyl ether causes the density to fall twice as much as in the case of p-chlorophenol. In the case of o-chlorophenol, as in that of all intermolecularly non-associated compounds, $\frac{d_{Cl,\ OH}}{d_{Cl}} < \frac{M_{Cl,\ OH}}{M_{Cl}}$, where M is the molecular weight, whereas in the case of m- and p-chlorophenols, as in that of all intermolecularly associated compounds, $\frac{d_{Cl,\ OH}}{d_{Cl}} > \frac{M_{Cl,\ OH}}{M_{Cl}}$. o-Chlorophenol also possesses a lower density than its isolog, o-chlorothiophenol (0.028 lower at 25°), whereas its isomer, m-chlorophenol, possesses, like all associated intermolecular compounds, a higher density than its isolog, m-chlorothiophenol (0.017 higher). Like other compound with an intramolecular hydrogen bond, o-chlorophenol also possesses much lower values of γ and η than the para-isomer (γ is 4.5 dynes/cm lower and η is 1.5 times lower at 131°); in passing to the methyl ethers the surface tension and viscosity of o-chlorophenol are only very slightly reduced, but those of the para-isomer are sharply reduced (at 131° γ falls by 7.4 dynes/cm as against 1.7 for the ortho-isomer, while η is reduced twice as against 1.2 times with the ortho-isomer). The boiling points of these compounds also exhibit a trend that is characteristic of associated inter- and intramolecular compounds: o-chlorophenol boils 42° lower than the para-isomer; its boiling point rises on transition to the methyl ether while that of p-chlorophenol falls (by 20°); in accord with the usual relations for boiling points of isologs, the boiling point of isologs, the boiling point point of o-chlorophenol is lower than that of its isolog, o-chlorothiophenol, while the intermolecularly associated m- and p-chlorophenols have higher boiling points than the corresponding thiophenols (respectively 10 and 12° higher).

The compounds in question also manifest the characteristics of inter- and intramolecularly associated compounds in the physical properties of their solutions (Table 2). In benzene and isoamyl acetate [13] the ortho-isomer gives solutions

* For Communication I see [1].

TABLE 1

Physical properties of chlorophenols and chloroanisoles

Compound		Density		Surface tension γ (dynes / cm)		Viscosity $\eta \cdot 10^5$		Boiling point
		131°	172°	131°	172°	131°	172°	
Chlorophenol	ortho	1.126	-	27.8	23.2	642	-	448°
	para	1.182	1.137	32.3	28.0	919	610	490
Chloranisole	ortho	1.074	1.020	26.2	21.5	504	383	468
	para	1.068	1.007	24.9	20.4	458	350	470

TABLE 2

Physical properties of solutions

Compound	Concentration	Solvent	Density d	Viscosity $\eta \cdot 10^5$ (25°)
o-Chlorophenol	1 g in 25 ml 0.01 N solution	Benzene	0.8555 (50°)	-
		Alcohol	0.7973 (50)	-
		Isoamyl acetate ...	0.9254 (25)	1202
p-Chlorophenol	1 g in 25 ml 0.1 N solution	Benzene	0.8584 (50)	-
		Alcohol	0.7980 (50)	-
		Isoamyl acetate	0.9289 (25)	1270

of the same concentration with lower density and viscosity than its para-isomer. The difference is extremely slight in alcohol, probably due to the appreciable destruction of the intramolecular hydrogen bond.

The available data for the physical properties of other halogenophenols also testify to the presence in their ortho-isomers of an intramolecular hydrogen bond right up to their boiling points. Thus, the d of o-bromophenol is appreciably lower than that of p-bromophenol (by 0.035 at 80°); $\frac{d_{Br,\ OH}}{d_{Br}} < \frac{M_{Br,\ OH}}{M_{Br}}$ (by 0.010), while in the case of p-bromophenol by contrast, $\frac{d_{Br,\ OH}}{d_{Br}} > \frac{M_{Br,\ OH}}{M_{Br}}$ (by 0.009). In the isolog series of the o-halogenophenols the density increases linearly with increasing molecular weight of the molecules (Fig. 1) [10], which would not have been the case if some of the members of the series were associated not internally, but intermolecularly. As with o-chlorophenol and other compounds with an intramolecular hydrogen bond, o-fluorophenol and o-bromophenol boil respectively 35 and 44° lower than their para-isomers; the methyl ether of o-bromophenol boils higher but the methyl ether of p-bromophenol boils lower than the respective starting phenols. In the isologous series of the o-halogenophenols, just as in other isologous series of normal (not intermolecularly associated) compounds, the difference in boiling points of the members of the series is governed in the main by the difference in polarizability (MR_D) of their molecules (Fig. 2). In the series of substituted compounds o-R(OH)X (where R is aryl and X is a substituent), however, the value of $b.p./(MR_D)^{1/3}$ changes regularly with the dipole moment of the molecules (Fig. 3); in this respect all the o-halogenophenols are subject to a dependence which is common to the series (the same constants characterizing the straight line), which would not have happened if some of them had been intermolecularly associated. In the latter event they ought to have given appreciable deviations from rectilinearity as is the case with the intermolecularly associated o-cresol and, in particular, pyrocatechol [1].

The intramolecular hydrogen bond of o-halogenophenols exercises on the properties of molecules and macromolecules, as a rule, an appreciably lower quantitative effect than the intramolecular O–H ...O bond in o-nitro- or o-acylphenols. This is because, compared with the latter types of compounds, the o-halogenophenols do not have the bands of their OH group shifted to such a great extent in the infrared spectrum in the long-wave direction, there is less inhibition of certain reactions (acetylation and formation of molecular compounds [14]), there is a greater tendency to rupture of the hydrogen bond during certain reactions and in certain solvents [15], and there is less difference in the values of certain physical constants between o- and p-isomers, o-hydroxy and o-methoxy compounds, etc. These characteristics of the compounds in question are usually accounted for by the greatly reduced stability of the O–H...Hal bond itself in comparison with the O–H...O bond. However, the changes in the properties of molecules and

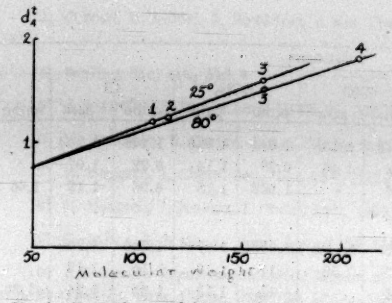

Fig. 1. Dependence of density of o-halogenophenols on molecular weight.
1 - F, 2 - Cl, 3 - Br, 4 - I.

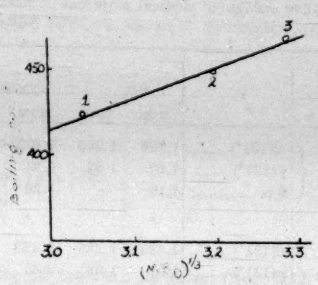

Fig. 2. Dependence of boiling point of o-halogenophenols on the polarizability of the molecules.
1 - F, 2 - Cl, 3 - Br.

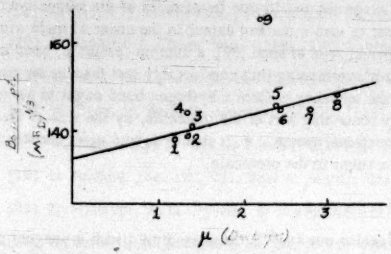

Fig. 3. Dependence of the ratio $\frac{b.p.}{(MR_D)^{1/3}}$ in the series o-$C_6H_4(OH)X$ (X = a substituent) on the dipole moment.
Values of X: 1 - F, 2 - Cl, 3 - Br, 4 - CH_3, 5 - OCH_3, 6 - $COCH_3$, 7 - CHC, 8 - NO_2, 9 - OH.

macromolecules caused by the presence of a hydrogen bond depend not only on its stability but also mainly on the nature of the atoms participating in its formation (their mass, size, structure of the electron shell, etc.), and on the size and shape of the resultant ring or complex, and on the accessibility of the individual atoms forming this bond to interaction with atoms of other molecules. Apart from this, the hydrogen bond itself is only one of the forms of interaction of atoms in a molecule, and its influence is superimposed on the conjugation effect and the induction effect. It is precisely for these reasons that it is impossible to evaluate the strength of the bond itself solely from the magnitude of the change in values of the constants brought about by the hydrogen bond or by interaction of the bonding atoms with molecules of solvent or reactant. These considerations also explain the above noted inconsistencies in the order of stability of the hydrogen bond with halogens in various reactions and solvents.

An inspection, however, of the relative change of physical properties (Table 3) reveals that the halogens behave like many other functional groups which form O–H...O bonds. On the other hand, the nearly complete agreement of the relative changes of properties on introduction of a given functional group in the para-position in phenol and anisole can be satisfactorily accounted for by the fact that intermolecular association of p-hydroxy compounds results in the formation in all cases of the same complexes as in the original phenol, namely those due to the O–H...O bond and not to the O–H...X bond.

Since all the halogens tend to form an intramolecular hydrogen bond, it is clear that the electronegativity of atoms cannot serve as a criterion of their ability to participate in the formation of a hydrogen bond. Other facts are consistent with this statement; for example, the highly negative nitrogen does not form a hydrogen bond in aliphatic amines [16]; on the other hand, carbon with its low electronegativity gives in the case of o-hydroxyphenylacetylene an intramolecular hydrogen bond of the type of O–H...C [17]. Moreover, the magnitude of the electronegativity itself (the tendency of the bonded atom to attract electrons) is not a specific and absolute property of the atom and varies with the partner of the bond [18]. The hypothesis of the decisive role of electronegative atoms in the formation of the hydrogen bond is a sequel to the concept of the ionic nature of the hydrogen bond, of its formation owing to the attraction of dipoles under the influence of electrostatic forces. In reality, however, the hydrogen bond is a real bond and not merely a bringing-together of molecules or atoms as the result of attraction or orientation of dipoles [19]. This is supported by

TABLE 3

Relative changes of physical properties $\frac{y_{C_6H_4(OR)X}}{y_{C_6H_5OR}}$

R	y	Substituent											
		NO_2		$COCH_3$		CHO		OCH_3		Cl		Br	
		ortho	para	ortho	para	ortho	para	ortho	para	ortho	para	ortho	para
H	d(131°)	1.220	1.289	1.037	1.113	1.065	1.155	1.041	1.080	1.146	1.204	-	-
	γ(131°)	1.07	1.52	0.97	1.32	0.88	1.45	0.96	1.14	0.92	1.07	-	-
	B.p.	1.18	-	1.20	1.62 (meta)	1.07	-	1.052	1.13	0.96	1.19	1.06	1.34
CH_3	d(131°)	1.289	1.296	1.113	1.131	1.155	1.102(?)	1.106	1.095	1.210	1.203	-	-
	γ(131°)	1.51	1.55	1.41	1.35	1.47	1.38	1.17	1.19	1.18	1.12	-	-
	B.p.	1.77	-	1.57	1.62	1.56	-	1.12	1.13	1.25	1.24	1.30	1.37

the X-ray data which show that the formation of the hydrogen bond is accompanied not by a simple approach but by a certain accumulation of electron clouds of the atoms bonded by the hydrogen bridge (the distance between the oxygens in the O–H...O bond is 0.3 A less than the sum of their van der Waals radii; the distance between the chlorine and the oxygen in the O–H...Cl bond [20] is 0.3 A less than the sum of the van der Waals radii of oxygen and chlorine). The reality of the hydrogen bond is also proved by the fact that its formation brings about marked changes in the properties of molecules: their dipole moment, energetic state of the electrons, oscillation frequencies of the respective functional groups, their chemical properties, etc, which would not occur to such a marked extent in the event of mere attraction of dipoles [21]. It is evident that the hydrogen bond is a special type of bond [22], a nuclear (protonic) bond in which the nucleus (proton) draws together two atoms, causing steady overlapping (but considerably less than in the case of a true chemical bond) of their electron clouds. In this case the tendency to form a hydrogen bond ought to be governed primarily by the polarity of the bonds of the atoms with the remaining part of the molecule, by the size of their electron cloud, and by the relative positions of the respective functional groups, i.e., it should depend upon the structure of the molecule as a whole and on the mutual influence of the atoms in the molecule.

EXPERIMENTAL

o-Chlorophenol was purified by distillation and by freezing out at +7°. Colorless liquid with a pungent phenolic odor, b.p. 173° (750 mm); p-chlorophenol was purified by repeated fractional distillation; colorless crystals, m.p. 37.5°; o- and p-chloroanisoles were prepared by treatment of the corresponding phenols with methyl iodide; colorless liquids with b.p. 198-199° (762 mm) and 194.8° (753 mm) respectively.

The density was determined in pyknometers with a capacity of approx. 10 ml; the viscosity was determined in the Ostwald viscosimeter with a period of efflux of water at 20° of 131 seconds; surface tension was determined by measurement of the pressure needed to enable a bubble of air to pass through. The procedure for measurement of the density of solutions has been described previously [11]. Our measured values of the η of chlorophenols are in close agreement with the literature data [23].

SUMMARY

1. The physical properties of chlorophenols and chloroanisoles testify to the ability of chlorine to give a stable intramolecular hydrogen bond even at the boiling point.

2. The molecular constants and physical properties of the halogenophenols show that all the halogens can form an intramolecular hydrogen bond.

3. The magnitude of the electronegativity of atoms cannot serve as a criterion of their tendency to form a hydrogen bond.

4. The theory is advanced that the hydrogen bond is a special type of nuclear (protonic), and not ionic, bond.

5. Values were determined of the density, surface tension and viscosity of o- and p-chlorophenols and anisoles at 131 and 172°, and also of the density of solutions in alcohol and benzene of o- and p-chlorophenols at 50°.

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THE HYDROGEN BOND AND THE PHYSICAL PROPERTIES OF SOME SUBSTITUTED PHENOLS AND ANISOLES

III. HYDROXYBENZOPHENONES

A.E. Lutsky

A difference in the character of association (inter- or intramolecular) of o- and p-acylphenols can be readily inferred from the data for their physical properties in the liquid or solid states (density, viscosity, surface tension, melting and boiling points, etc.) [1]. In this connection determinations were made of the density (d), surface tension (γ) and viscosity (η) at 131 and 172° (or 182°) of the following compounds: benzophenone, o- and p-hydroxybenzophenones, benzoyl and acetyl derivatives of phenol, phenol, acetophenone, and o- and p-hydroxyacetophenones (table). The table also compares the melting points of the compounds in question.

Physical properties of acyl substituted phenols and phenol derivatives

Compound	d		γ (dynes/cm)		$\eta \cdot 10^5$		Melting point
	131°	172°	131°	172°	131°	172°	
Benzophenone	-	0.985	-	29.1	-	766	300°
Hydroxybenzophenone:							
o-	-	1.030	-	28.3	-	800	314
p-	-	1.133	-	37.6	-	4859	407
Acetophenone	0.927	0.878 (184°)	26.7	22.1 (184°)	420	329 (184°)	293
Hydroxyacetophenone:							
o-	1.018	0.962 (184°)	29.2	24.2 (184°)	701	465 (184°)	-
p-	1.092	1.047 (184°)	39.7	35.1 (184°)	3576	1770 (184°)	382
Phenol	0.981	-	30.0	-	725	-	314
Phenyl acetate	0.970	0.901 (184°)	25.7	19.6 (184°)	572	365 (184°)	-
Phenylbenzoate	1.041	1.004 (184°)	31.6	26.8 (184°)	1113	738 (184°)	343

It follows from the enumerated values that p-hydroxybenzophenone manifests all the features typical of compounds which are intermolecularly associated: introduction of the OH group causes the values of all properties to increase but not in the same degree, as would have resulted only with change of mass, dipole moment and polarizability of the molecules. Thus the viscosity rises approximately 6 times, the melting point by 107°, while the relative increase of density appreciably exceeds the rise in molecular weight, i.e., $\frac{d_{COC_6H_5OH}}{d_{COC_6H_5}} > \frac{M_{COC_6H_5OH}}{M_{COC_6H_5}}$ (by 0.062). Compared with its isomer (phenyl benzoate) p-hydroxybenzophenone possesses appreciably higher values of d (1.12 times), γ (1.4 times), η (nearly 6.5 times) and m.p (64° higher). Unlike p-hydroxybenzophenone, o-hydroxybenzophenone behaves like all normal, non-associated compounds. Thus, in comparison with benzophenone it possesses slightly higher values of properties in correspondence with its higher molecular weight, polarizability and molecular size. It has the same melting point as phenol. The relative increase in its density $\frac{d_{COC_6H_5OH}}{d_{COC_6H_5}}$ lags behind the relative increase in molecular weight (by 0.043). Like other normal compounds, o-hydroxybenzophenone has nearly the same values of all its properties as its isomer, phenyl benzoate.

All the relations mentioned above are similar not only qualitatively but also nearly quantitatively to those observed in the case of hydroxyacetophenones, for which numerous investigations have established that the ortho-isomer is intramolecularly associated and the para-isomer intermolecularly associated. In comparison with acetophenone, p-hydroxyacetophenone possesses a 1.6 times higher density, a 5.5 times higher viscosity, and a 1.5 times greater surface tension;

its melting point is 89° higher. Approximately the same differences are also found when we compare p-hydroxyacetophenone with its isomer, phenyl acetate. In respect of all its properties, o-hydroxyacetophenone only differs to an insignificant extent (in the direction of higher values due, evidently, to its higher dipole moment) both from acetophenone and from phenyl acetate. On this basis we can conclude that also the difference in properties between o- and p-hydroxy benzophenones is caused not by the steric factor but by a difference in the character of their association: the presence in the former of an intramolecular and in the latter of an intermolecular hydrogen bond.

The data set forth in the table permit a comparison of the influence of the effect of formation of an ether and an ester on the physical properties of liquids. Transition from phenol to anisole causes, owing to loss of the ability to associate intermolecularly, an appreciable fall in the values of all the properties considered (at 131° $\underline{d}$ falls by 0.094, γ by 7.9 dynes/cm, and η 1.8 times). The same trend, although not quite so marked, is observed on formation of phenyl acetate ($\underline{d}$ lower by 0.011, γ by 4.3 dynes/cm, and η by a factor of 1.3). With phenyl benzoate, compared with phenol, however, the values of the properties do not decrease, but increase. This is evidently because the introduction into the molecule of the original phenol in place of hydrogen of a functional group brings about an appreciable rise in molecular weight, size and polarizability. This slightly lowers in the case of acetyl the effect of elimination of association, while in the case of benzoyl it even overlaps with it. This type of phenomenon is also observed in the formation of ethers, when the lengthening of the hydrocarbon chain of the alkyl (replacing the hydrogen of the hydroxyl) is accompanied by a reduction in the difference between the physical properties of the original hydroxy compounds and the ether, while at a certain length of this chain the formation of an ether is already accompanied not by a fall but by a rise in the values of the properties.

EXPERIMENTAL

Acetophenone was purified by repeated fractional distillation; benzophenone was purified by recrystallization from alcohol; m.p. 48°. Phenyl acetate was prepared from phenol by acetylation by Chattaway's method [2]; colorless liquid with b.p. 192-192.5°. Phenyl benzoate was prepared by the benzoylation of phenol; after two recrystallizations from alcohol it formed white crystals with m.p 70°. o- and p-Hydroxyacetophenones were prepared by Fries rearrangement from phenyl acetate. o-Hydroxyacetophenone was purified by redistillation in vacuum, and p-hydroxyacetophenone by recrystallization from water. o- and p-Hydroxybenzophenones were prepared by the method of Sandulesco and Girard [3]; after purification by recrystallization from alcohol and water, the former gave light-yellow crystals with m.p. 41°, and the second gave colorless crystals with m.p. 134°. The methods of determination of density, viscosity and surface tension have been previously described [1, 4].

SUMMARY

Values were determined of the density, viscosity and surface tension of phenol and six of its substituted compounds and derivatives, also of acetophenone at 131, 172 or 184°. The special features of the association of these compounds are discussed.

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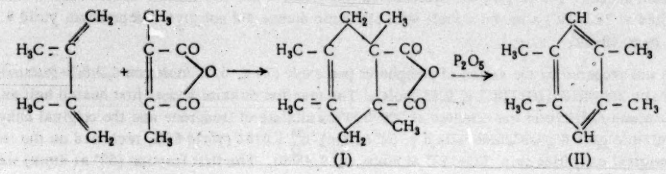
SYNTHESIS OF HYDROCARBONS

XLVIII. TETRAMETHYLBENZENES FROM ADDUCTS OF ALKADIENES WITH PYROCINCHONINIC ANHYDRIDE

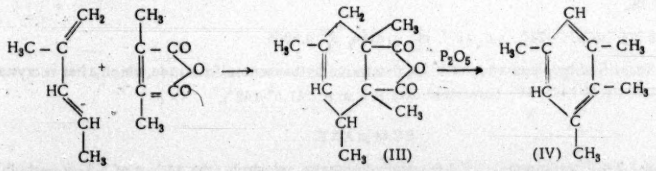
V.R. Skvarchenko, R.Ya. Levina and T.V. Kostrova

The present paper describes work in continuation of the preceding investigations on the synthesis of aromatic hydrocarbons from dienic hydrocarbons (reaction between phosphorus pentoxide and adducts of these hydrocarbons with maleic [1], methylmaleic [2] and dimethylmaleic [3] anhydrides). We have now effected the preparation of two tetramethylbenzenes: durene (1,2,4,5-tetramethylbenzene) and isodurene (1,2,3,5-tetramethylbenzene).

Reaction of phosphorus pentoxide with 1,2,4,5-tetramethyl-1,2,3,6-tetrahydrophthalic anhydride (I) – the adduct of 2,3-dimethyl-butadiene-1,3 with dimethylmaleic (pyrocinchoninic) anhydride – gave durene (II) (yield 45%), which was identified by its melting point and by the melting point of its mixture with authentic durene.



The reaction between phosphorus pentoxide and 1,2,3,5-tetramethyl-1,2,3,6-tetrahydrophphalic anhydride (III) the adduct of 2-methylpentadiene-1,3 with pyrocinchoninic anhydride – gave isodurene (IV) (ield 62%, reckoned on the adduct entering into reaction). *



The prepared isodurene was identified from its constants and from the melting point of its sulfonamide.

EXPERIMENTAL

1. Preparation of Adducts of Dienic Hydrocarbons with Pyrocinchoninic Anhydride – Tetramethyltetrahydrophthalic Anhydride

1,2,4,5-Tetramethyl-1,2,3,6-tetrahydrophthalic anhydride (I) was prepared by heating 2,3-dimethyl-1,3 (23 g, 0.28 mole) with pyrocinchoninic anhydride ** (27 g, 0.21 mole) in an autoclave at 170-180° for 20 hours. After distillation of unreacted diene and distillation of the residue, an adduct was obtained with b.p 115° (5 mm), which after recrystallization from ligroin melted at 76.5°.

6.468 mg substance: 16.450 mg CO_2; 4.600 mg H_2O. 5.200 mg substance: 13.191 mg CO_2; 3.690 mg H_2O. Found %: C 69.41, 69.23; H 7.95, 7.94. $C_{12}H_{16}O_3$. Calculated %: C 69.21; H 7.74.

The yield of adduct was 40 g (90%).

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* The adduct of 2-methylpentadiene-1,3 with pyrocinchoninic anhydride was partly recovered unchanged after reaction.

** Pyrocinchoninic anhydride with m.p. 96° was prepared by distillation of dimethylmalic acid, in turn prepared from ethylacetoacetate [4].

Adduct of 2,3-dimethylbutadiene-1,3 with pyrocinchoninic anhydride has not been described in the literature.

1,2,3,5-Tetramethyl-1,2,3,6-tetrahydrophthalic anhdride (III) was prepared by heating in an autoclave, at 140-160° for 15 hours, pyrocinchoninic anhydride (46 g, 0.37 mole) with a mixture (46 g, 0.56 mole) of 2-methylpentadiene-1,3 and 2-methylpentadiene-2,4.* (After driving off the unreacted 2-methylpentadiene-2,4** (11 g, b.p. 76.3° at 762 mm, n_D^{20} 1.4520 [5]) and pyrocinchoninic anhydride (9 g) and distilling the residue, an adduct was obtained with the following characteristics:

B.p. 120°(4 mm), n_D^{20} 1,4850, d_4^{20}1.1037, MR_D 54.02. $C_{12}H_{16}O_3$ f. Calculated 54.40.
7.069 mg substance: 18.003 mg CO_2; 4.973 mg H_2O. 5.886 mg substance: 14.987 mg CO_2; 4.204 mg H_2O.
Found %: C 69.50, 69.49; H 7.87, 7.99. $C_{12}H_{16}O_3$. Calculated %: C 69.21; H 7.74.

The yield of adduct was 44 g (72%, reckoned on the reacted anhydride).

The adduct of 2-methylpentadiene-1,3 with pyrocinchoninic anhydride has not been described in the literature.

2. Interaction of tetramethyltetrahydrophthalic anhydrides with phosphorus pentoxide

Durene (II). Into a Wurtz flask (250 ml capacity), fitted with a condenser and a thermometer reaching nearly to the bottom of the flask, were charged 1,2,4,5-tetramethyl-1,2,3,6-tetrahydrophthalic anhydride (30 g, 0.145 mole) and phosphorus pentoxide (20.5 g, 0.145 mole). The reaction mixture was gradually heated to 330°; the durene formed distilled off during the process and was then heated (under reflux) with 40% sodium hydroxide solution for removal of any admixed unreacted adduct. The so-purified hydrocarbon was distilled off with steam. After recrystallization from alcohol, durene melted at 78.5-79°; a mixed sample with authentic durene did not give a depression; yield 8.7 g (45%). Literature data [7]: m.p. 79-80°.

Isodurene (IV) was prepared by the action of phosphorus pentoxide (10 g, 0.07 mole) on 1,2,3,5-tetramethyl-1,2,3,6-tetrahydrophthalic anhydride (III) (14.7 g, 0.07 mole). The reaction mixture was at first heated half an hour at 150-180°, *** after which distillation was effected at 200-300° of a mixture of isodurene and the original anhydride. Distillation of this mixture gave 6 g isodurene with b.p. 52° (4mm), n_D^{20} 1.5120 (yield 62%, reckoned on the reacted anhydride), and 5 g original anhydride (b.p. 120-125° at 5mm, n_D^{20} 1.4880). The first fraction (52° at 4mm) was boiled with 40% sodium hydroxide solution and steam distilled. The distilled isodurene was dried with calcium chloride and distilled in a nitrogen stream over sodium:

M.p. −26-24°, b.p. 70.5-71° (8 mm), 196-197° (745 mm) n_D^{20} 1.5129, d_D^{20} 0.8882, MR_D 44.70. $C_{10}H_{14}$ f. Calculated 44.78.

Literature data [8]: m.p. −24°; b.p. 197°, n_D^{20} 1.5134, d_4^{20} 0.8906.

Isodurene was identified by preparation of 2,3,4,6-tetramethylbenzenesulfonamide, which, after recrystallization from dilute alcohol, melted at 140-141° (literature data [9]: m.p. 141.5°-142°).

SUMMARY

1. Cleavage of 1,2,4,5-tetramethyl-1,2,3,6-tetrahydropthalic anhydride (the adduct of 2,3-dimethylbutadiene-1,3 with pyrocinchoninic anhydride) by heating with phosphorus pentoxide gave durene (1,2,4,5-tetramethylbenzene) in a yield of 45%.

2. From 1,2,3,5-tetramethyl-1,2,3,6-tetrahydrophthalic anhydride (adduct of 2-methylpentadiene-1,3 with pyrocinchoninic anhydride) was obtained isodurene (1,2,3,5-tetramethylbenzene) in a yield of 62%, reckoned on the reacted anhydride.

3. For the first time adducts have been prepared of pyrocinchoninic anhydride with butadiene homologs – 2,3-dimethylbutadiene-1,3 and 2-methylpentadiene-1,3.

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* The mixture of 2-methylpentadiene-1,3 and 2-methylpentadiene-2,4 (b.p. 72.5-76° at 758 mm; n_D^{20} 1.4475) was obtained by dehydration of dimethylallylcarbinol [5].

** 2-Methylpentadiene-2,4 does not react with maleic anhydride [6] and, as shown in the present research, it does not react with pyrocinchoninic anhydride.

*** Without previous heating (at 150-180°) of the reaction mixture, 50% of the original ahhydride was distilled off together with the isodurene, the yield of which in this case was only 33%, reckoned on the anhydride entering into reaction.

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* See C.B. Translation, p. 2113.
** " " " " p. 251.

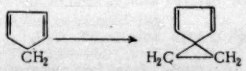
SYNTHESIS OF HYDROCARBONS

SPIRO-(2,4)-HEPTADIENE-1,3 AND SPIRO-(2,4)-HEPTANE

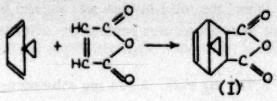
R. Ya. Levina, N.N. Mezentsova and O.V. Lebedev

In one of our previous communications [1] we described a new method of synthesis of spiro-(4,4)-nonane – the interaction of sodium cyclopentadiene with 1.4-dibromobutane, followed by hydrogenation of the product of this reaction – spiro-(4,4)-nonadiene-1,3 – to spiro-(4,4)-nonane.

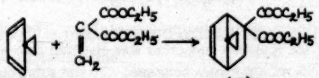
In the present work this simple reaction was applied to the synthesis of another bicyclic hydrocarbon of the spiran series: spiro-(2,4)-heptadiene-1,3. From the latter by hydrogenation was obtained spiro-(2,4)-heptane. For this purpose ethylene bromide was brought into reaction with sodium cyclopentadiene (prepared by the action of sodium in liquid ammonia on cyclopentadiene*):



The yield of spiroheptadiene was 25% of the theoretical, reckoned on the ethylene bromide. The dienic nature of the obtained hydrocarbon (presence of a conjugated series of double bonds) was confirmed by preparation of the adduct with maleic anhydride and also with methylenemalonic ester:

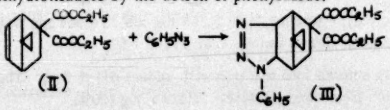


(I)



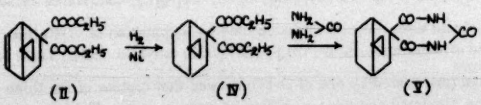
(II)

The liquid adduct with methylmalonic ester (II) (1,1-dicarbethoxy-2,5-endocyclopropylidenecyclohexene-3), was converted into a crystalline dihydrotriazole by the action of phenylazide:



(II) (III)

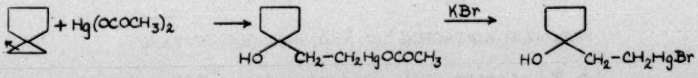
This reaction demonstrated the presence of an endomethylene bridge in the cyclic ester. The adduct of spiroheptadiene with methylenemalonic ester (II) was hydrogenated over skeletal nickel, and the resultant 1,1-dicarbethoxy-2,5-endocyclopropylidenecyclohexane (IV), a disubstituted malonic ester, was transformed by reaction with urea into a "bridged spiro-barbituric" acid (V):



(II) (IV) (V)

* A secondary product of this reaction was cyclopentene, which was formed during partial reduction of cyclopentadiene with sodium in liquid ammonia; cyclopentene was identified by preparation of its dibromide – 1,2-dibromocyclopentane.

Hydrogenation of spiro-(2,4)-heptadiene-1,3 over skeletal nickel gave spiro-(2,4)-heptane in a yield of 58% of the theoretical. The presence of a three-membered ring in the resultant spiropentane (VI) was established by its reaction with mercury acetate*:



Investigation of the Raman spectrum of the prepared spiroheptane (VI) also confirmed the presence of three- and five-membered rings.

Ya. M. Slobodin [3] recently described the synthesis of spiro-(2,4)-heptane by another method in which spriohepteane is formed in a mixture with methylenecyclohexane.

EXPERIMENTAL

Spiro-(2,4)-heptadiene-1,3 was prepared by the action of ethylene bromide (1.15 g) on sodium cyclopentadiene (40 g cyclopentadiene and 28 g sodium) in liquid ammonia by the method previously described by us [1] for the synthesis of spiro-(4,4)-nonadiene-1,3. The prepared hydrocarbon was distilled in vacuum in a nitrogen stream and after a second distillationhad the following constants:

B.p. 57° (100 mm), n_D^{20} 1.5078, d_4^{20} 0.8999, MR_D 30.57. C_7H_8 F 2. Calculated** 29.89; EM_D 0.68.

The yield of spiroheptadiene was 14 g (25%). From four repeated experiments was obtained 58 g hydrocarbon. Spiroheptadiene has not been described in the literature.

The adduct of spiro-(2,4)-heptadiene-1,3 (3.5 g) with maleic anhydride (3.7 g) was prepared under the usual conditions of the diene synthesis (in anhydrous ether). The reaction mixture heated up appreciably and crystals of the adduct (I) came down. After driving off the ether, the solid residue was worked up with hot water (for removal of unreacted maleic anhydride) and dried in a desiccator over phosphorus pentoxide; after two recrystallizations from ligroin the adduct had m.p. 97°, yield 6.4 g, (89%).

5.585 mg substance: 14.315 mg CO_2; 2.710 mg H_2O. 3.805 mg substance: 9.765 mg CO_2; 1.820 mg H_2O. Found %: C 69.95, 70.04; H 5.43, 5.35. $C_{11}H_{10}O_3$. Calculated %: C 69.47, H 5.30.

Adduct of spiroheptadiene 1,3 with methylenemalonic ester (II). The solid polymer of methylenemalonic ester*** (12 g) was depolymerized by heating the resultant monomer was distilled into a three-necked flask fitted with a stirrer and reflux condenser and containing 20 ml anhydrous benzene. To the solution was then added an equimolecular amount (6 g) of spiroheptadiene. The reaction mixture heated up considerably. After two-hours' heating on a water bath, the adduct (II) was vacuum-distilled:

B.p. 138-139° (9 mm), n_D^{20} 1.4790, d_4^{20} 1.0879, MR_D 68.89. $C_{15}H_{20}O_4$ F. Calculated 68.41. Yield 9 g (50%).

4.427 mg sub.: 11.063 mg CO_2; 3.084 mg H_2O. 5.966 mg sub.: 14.948 mg CO_2; 4.241 mg H_2O. Found %: C 68.20, 68.37; H 7.79, 7.95. $C_{15}H_{20}O_4$. Calculated %: C 68.18; H 7.57.

Phenylazide (0.6 g) readily entered into reaction with adduct (II) (1.3 g). The resultant N-phenyltriazole (III) had m.p. 141° (after recrystallization from ethyl acetate). Yield 1.7 g (90%).

5.629 mg substance: 0.565 ml N_2 (24°, 744 mm). 5.405 mg substance: 0.536 ml N_2 (24°, 744 mm). Found %: N 11.30, 11.18. $C_{21}H_{25}O_4N_3$. Calculated %: N 10.97.

Hydrogenation of adduct (II) (5.2 g) in the cold, over skeletal nickel in anhydrous alcohol led to formation of 1,1-dicarbethoxy-2,5-endocyclopropylidenecyclohexane (IV):

B.p. 160° (16 mm), n_D^{20} 1.4675, d_4^{20} 1.0687, MR_D 69.28. $C_{15}H_{22}O_4$. Calculated 68.90. Yield 4.2 g (84%).

This disubstituted malonic ester (IV) was characterized by preparation of crystalline "spirobarbituric" acid (by the action of urea in presence of sodium ethoxide); m.p. 250° (from ethyl alcohol). Yield 55% of the theoretical.

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* A study of this reaction (discovered by one of us [2]) showed that rupture of the three-membered ring takes place at the bond between the most alkylated and the non-alkylated carbon atoms. This regularity (established in several experiments) also determines the structure of the γ-mercurated alcohol (prepared by us) as 1-(β-bromomercuriethyl)-cyclopentanol-1.

** The high constants and the occurrence of exaltation of molecular refraction were evidently due to the structure of spiroheptadiene being similar to a certain degree to that of the fulvene hydrocarbons.

*** For spiroheptadiene, as for all its derivatives, the increment of the 3-membered ring (0.7) was added to the calculated MR_D.

4.882 mg-substance: 0.507 ml N_2 (27°, 745.3 mm) 5.047 mg-substance: 0.519 ml N_2 (27°, 750 mm). Found %: N 11.53, 11.55. $C_{12}H_{14}O_3N_2$. Calculated %: N 11.95.

Spiro-(2,4)-heptane

Spiroheptadiene (12 g) was hydrogenated in the cold in presence of skeltal nickel (in 50 ml anhydrous alcohol). A mixture of hydrocarbon and alcohol was taken off from the alcoholic solution through a column at 64-78°. The hydrocarbon was separated with water, dried with calcium chloride and distilled over sodium. Yield 7 g (58%). Distillation in a column of 15 g hydrocarbon gave spiro-(2,4)-heptane with the following constants:

B.p. 98.0-98.5° (743 mm), n_D^{20} 1.4390, d_4^{20} 0.8106, MR_D 31.21. C_7H_{12}. Calculated MR_D 30.82.
8.393 mg substance: 26.937 mg CO_2; 9.489 mg H_2O. 7.442 mg substance: 23.901 mg CO_2; 8.312 mg H_2O. Found %: C 87.59, 87.65; H 12.38, 12.50. C_7H_{12}. Calculated %: C 87.50; H 12.50.

The prepared spiro-(2,4)-heptane was examined by Raman spectroscopy:*

218 (1.5); 276 (0.8); 295 (1); 339 (1); **387-397**; (2;b); 454 (1); 499 (12;b); 586 (0); 635 (0.5); 671 (0.5); 718 (2;b); 786 (3;b); 839 (2.5); **896 (12)**; 953 (30); 970 (1); 999 (2); **1022 (4)**; 1094-1196 (1 b); 1227 (25); 1270-96 (20 b); 1352 (6); 1382 (2.5); 1427 (2); 1440 (10); 1465 (2).

The above data show that the spectrum of spiro-(2,4)-heptane contains intense lines characteristic of a five-membered ring (printed in bold type) and of a three-membered ring:

339 (1); 499 (12;b); 718 (2;b); 786 (3;B); 839 (2.5); 953 (30); 1227 (25);

The three- membered ring in spiroheptane (0.5 g) was readily broken by the action of mercuric acetate (1.6 g in 7 ml water [5]) on the hydrocarbon. The resultant organomercury compound was extracted with ether; the ether was driven off and the residue of viscous oil dissolved in 75 ml water; to the solution, after cooling, was added a solution of an equimolecular amount (0.6 g) of potassium bromide in 100 ml water. A white precipitate of 1-(β-bromomercuriethyl) cyclopentanol-1 came down and after recrystallization from ligroin had m.p. 70°. Yield 0.7 g (34%).

9.164 mg substance: 7.110 mg CO_2; 2.795 mg H_2O. Found %: C 21.17; H 3.41. $C_7H_{13}OBrHg$. Calculated %: C 21.12; H 3.30.

SUMMARY

1. Reaction of sodium cyclopentadiene in liquid ammonia with ethylene bromide gave spiro-(2,4)-heptadiene-1,3, which on hydrogenation gave spiro-(2,4)-heptane.

2. Spiro-(2,4)-heptadiene-1,3 was characterized as the adducts with maleic anhydride and methylenemalonic ester.

3. The presence in spiro-(2,4)-heptane of a three-membered ring was proved by cleavage under the action of mercuric acetate, as well as by examination of its Raman spectrum.

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Moscow State University

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** T. p. = C. B. Translation pagination.

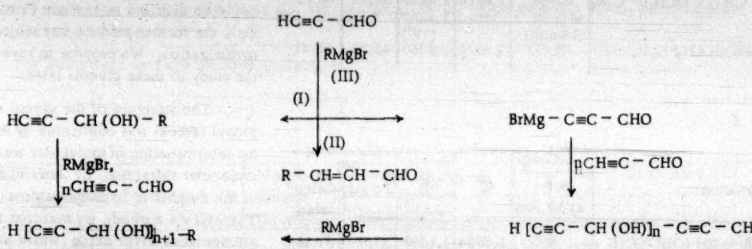
REACTION OF PROPIOLALDEHYDE WITH ORGANOMAGNESIUM COMPOUNDS

A. A. Petrov

Until recently propiolaldehyde (propargylaldehyde) was an extremely inaccessible substance. The position changed only after development of a new industrial method of preparation of 2-propyn-1-ol from acetylene and formaldehyde [1] and of a method of oxidation of this alcohol to the aldehyde [2]. Nevertheless many interesting transformations of propiolaldehyde have already been reported in the literature: polymerization [2, 3], hydrogenation [4], hydration [5], reactions with diazo compounds [3, 6], etc. Up to now, however, investigators have neglected their reactions with organomagnesium compounds.

We were interested in the possibility of using this aldehyde as a starting point for the preparation of alkyl propargylaldehydes ($CH{\equiv}C-CH(OH)-R$), which in turn were of interest as possible starting points for the preparation of the little investigated enynic hydrocarbons. Isolated representatives of this series of alcohols have been described in the literature; they were usually obtained by reaction of metallic acetylides with aldehydes [7-12] or by the action of caustic alkali on the corresponding olefinic haloalcohols [12].

The reaction of propiolaldehyde with Grignard reagents could proceed in three main directions (see scheme below), since this aldehyde contains two reactive groups and a conjugated system of multiple bonds.



The principal products of the reaction could be: 1) alkyl propargyl alcohols; 2) unsaturated aldehydes of the type of crotonaldehyde; and 3) organomagnesium compounds of the type of acetylides. These initial products could give products of more far-reaching condensation with the starting substances. Acetylenic alcohols could be formed by reaction with excess of Grignard reagent, and then the aldehyde entering the reaction zone could give diacetylenic glycols; the latter (by the same scheme) could then lead to polyacetylenic monohydric alcohols. Further reaction of organomagnesium derivatives of propiolaldehyde with the same aldehyde could lead to di- and polyalkylacetylenic hydroxaldehydes. Moreover, we could expect formation of products of interaction between all the substances obtained by the three schemes outlined.

In practice, the products of the reaction consisted of two main substances and small amounts of first-runnings and resinous residue. The main substances were alkyl propargyl alcohols and diacetylenic glycols. Aldehydes were not present among the reaction products: not one of the fractions gave derivatives with p-nitrophenylhydrazine. The small initial fraction reacted with reagents for the acetylenic bond and hydroxyl group. Due to their small amounts they could not be fractionated and studied.

Alkylpropargyl alcohols were easily separated from the reaction mixture in the pure form; they differed little in constants from specimens previously obtained by other routes. It is seen from Table 1 that the molecular refraction found for all the substances is in good agreement with the calculated value. The homologous difference in boiling points is slightly increased in the homologous series and amounts to 15-20°.

Alkylpropargyl alcohols readily reacted with ammoniacal silver oxide (white precipitate), were easily acetylated, and slowly combined with one molecule of bromine in chloroform solution. The constants of the acetates are set forth in Table 2 and those of the dibromides in Table 3. The dibromides were light-yellow liquids with an odor of conifers.

TABLE 1

Substance	Boiling point at 20 mm	Boiling point at 755 mm	d_4^{20}	n_D^{20}	MR Found	MR Calculated
$HC\equiv C-CH(OH)-CH_3$	-	108-109°	0.8942	1.4275	20.14	20.20
		106.5-107.5	0.8858	1.4265	20.29	20.20 [12]
$HC\equiv C-CH(OH)-C_2H_5$	-	124-125	0.8850	1.4350	24.80	24.81
	-	125	0.8926 (15°)	1.4347 (15°)	24.57	24.81 [12]
$HC\equiv C-CH(OH)-C_3H_7$	58-58.5°	141-141.5	0.8722	1.4370	29.41	29.43
	-	140-141	0.8704	1.4330	29.22	29.43 [9, 10, 12]
				1.4382 (16.5°)		
$HC\equiv C-CH(OH)-C_3H_7$-iso	-	131-132	0.8779	1.4357	29.21	29.43 [7]
$HC\equiv C-CH(OH)-C_4H_9$	72-72.5	161.5-162.5	0.8366	1.4412	34.19	34.05
$HC\equiv C-CH(OH)-C_4H_9$-iso	65-66	151.5-152	0.8518	1.4380	34.18	34.05

TABLE 2

Substance	Boiling point at 20 mm	d_4^{20}	n_D^{20}	MR Found	MR Calculated
$HC\equiv C-CH(OCOCH_3)-CH_3$	37.5-38°	0.9488	1.4152	29.60	29.56
$HC\equiv C-CH(OCOCH_3)-C_2H_5$	50.5-51.5	0.9343	1.4200	34.17	34.18
$HC\equiv C-CH(OCOCH_3)-C_3H_7$	65-66	0.9210	1.4238	38.82	38.80
	65.5-66 (19 mm)	—	1.4257 (19°)	—	— [10]
$HC\equiv C-CH(OCOCH_3)-C_4H_9$ iso	71-72	0.9072	1.4260	43.55	43.41

TABLE 3

Substance	Boiling point at 10 mm	d_4^{20}	n_D^{20}	MR Found	MR Calculated
$CHBr=CBr-CH(OH)-CH_3$	91°	1.9995	1.5598	37.08	37.26
$CHBr=CBr-CH(OH)-C_2H_5$	98-99	1.8600	1.5488	41.71	41.87
$CHBr=CBr-CH(OH)-C_3H_7$	108-109	1.7485	1.5374	46.00	46.49
$CHBr=CBr-CH(OH)-C_4H_9$	118-119	1.6306	1.5310	51.61	51.11

We did not succeed, except in two cases, in isolating in the pure state the members of the second main group of reaction products – the diacetylenic glycols: an attempt to distil them in vacuum (3 mm) caused violent decomposition. In the distillation flask remained a hard, porous, carbonaceous mass. Only the glycols with propyl and butyl radicals could be distilled in vacuum (3 mm). Only the former product was subjected to investigation. We propose to revert to the study of these glycols later.

The structure of the glycol with a propyl radical was confirmed by analyses, by determination of molecular weight and molecular refraction, by determination of the number of hydrogen atoms (A.P. Terentyev's method), by reaction with ammoniacal silver oxide (white precipitate, rapidly turning black), and by data for hydrogenation in presence of collodial palladium. In the last case, the addition of the first two molecules of hydrogen takes place very quickly. The third molecule adds on very much more slowly. The final portion of hydrogen was absorbed with great difficulty.

Diacetylenic glycols could be obtained either according to scheme I as a result of interaction with the Grignard reagent and then with the original aldehyde of the alkylpropargyl alcohols, or according to scheme II as a result of primary formation from propiolaldehyde of an acetylide followed by reaction with excess of Grignard reagent. The first route seemed to us more probable, since the aldehyde group is undoubtedly more active than acetylenic hydrogen with respect to organomagnesium compounds. Probably only the alcoholate of the acetylenic alcohol is initially formed, and it then reacts with excess Grignard reagent with substitution of hydrogen. The propiolaldehyde entering the reaction zone reacts both with the original magnesium alkyl halide and with the acetylenic alcohol. This theory of the course of the reaction is confirmed by the fact that when it is carried out more quickly and at lower temperatures, the yield of acetylenic alcohol is increased, while that of diacetylenic glycol is reduced.

The residues after distillation of the diacetylenic glycols are evidently polyacetylenic monohydric alcohols. Their isolation in the pure state is only possible in high vacuum.

Consequently, this investigation has established the possibility of preparation from propiolaldehyde of alkylpropargyl alcohols and diacetylenic glycols in adequately high yield by the normal reaction of this aldehyde with Grignard reagents.

EXPERIMENTAL

Propiolaldehyde was prepared by oxidation of 2-propyn-1-ol (propargyl alcohol) with bichromate under the previously described conditions [2]. Rapid performance of the reaction resulted in an increased yield of aldehyde (up to 50-55%).

Propioladehyde had the constants:
B.p. 54-55° (742 mm), d_4^{20} 0.9152, n_D^{20} 1.4070, MR 14.54. C_3H_2O F. Calculated 14.06. The literature reports b.p. 53-55° [2].

The reaction of propiolaldehyde with organomagnesium compounds was carried out under the following conditions.

To a solution (cooled with a mixture of ice and salt) of Grignard reagent, prepared from 0.6 g-atom magnesium, was carefully added a 50% solution of 0.5 mole aldehyde in anhydrous ether. In the case of methyl magnesium bromide, the reaction products for the most part remained in solution; in the case of ethyl magnesium bromide they were almost completely located in the precipitate; in the case of higher halides they were distributed between precipitate and solution. The reaction product was poured on to ice mixed with a saturated solution of ammonium chloride. The mixture was then (for breaking of the emulsion) acidified with 25% sulfuric acid. The ether layer was washed with a solution of sodium carbonate and dried over sodium sulfate. The aqueous layer was extracted with ether in an extractor fitted with a stirrer. In the case of lower alcohols the extraction of the aqueous layer yielded a considerable amount of substance. The ether was driven off at normal pressure on a water bath, and the reaction product was distilled in vacuum (distillation at normal pressure leads to violent decomposition of the substance). After a volatile fraction had come over, the temperature rose rapidly and the diacetylenic glycol started to come over at constant temperature. The process of distillation of the glycol in nearly every case was accompanied by violent decomposition with complete carbonization of the residue and contamination of the distillate.

Alkylpropargyl alcohols were isolated from the light fractions by distillation at normal pressure in a Widmer column. Their yields varied sharply with the experimental conditions. With good cooling and rapid working they amounted (in %) to: methylpropargyl 60-65, ethylpropargyl 35-40, propylpropargyl 20-25, butylpropargyl 15-20 and isobutylpropargyl 35-40.

The analytical data are set forth in Table 4.

TABLE 4

Substance	Weight of sample (in mg)	Weight (in mg)		Found (%)		Calculated (%)	
		CO_2	H_2O	C	H	C	H
$HC\equiv C-CH(OH)-CH_3$	14.02	35.21	10.70	68.54	8.54	68.54	8.63
$HC\equiv C-CH(OH)-C_2H_5$	18.74	49.09	15.71	71.48	9.38	71.40	9.59
$HC\equiv C-CH(OH)-C_3H_7$	15.04	40.35	13.94	73.21	10.37	73.43	10.27
$HC\equiv C-CH(OH)-C_4H_9$	12.06	33.06	11.77	74.81	10.92	74.95	10.83
$HC\equiv C-CH(OH)-C_4H_9$-iso	20.20	55.70	19.85	75.25	10.99	74.95	10.83
$HC\equiv C-CH(OCOCH_3)-CH_3$	11.91	27.90	8.02	63.93	7.53	64.26	7.19
$HC\equiv C-CH(OCOCH_3)-C_2H_5$	11.26	27.60	8.44	66.89	8.39	66.64	7.99
$HC\equiv C-CH(OCOCH_3)-C_3H_7$	11.33	28.30	8.71	68.16	8.60	68.54	8.63
$HC\equiv C-CH(OCOCH_3)-C_4H_9$-iso	11.38	29.07	9.70	69.71	9.54	70.10	9.15

Acetylation of alkylpropargyl alcohols was conducted with acetyl chloride (20% excess) in pyridine (three times the amount of alcohol) with cooling. The reaction mixture was worked up in the usual way. The analytical data for the acetates are set forth in Table 4.

Dibromides were obtained by addition of bromine in chloroform solution to four alkylpropargyl alcohols. Yields 70-80%. The dibromides of the first three homologs distilled at 10 mm almost without decomposition. Higher homologs required a lower pressure. Analytical data for the dibromides appear in Table 5.

The yield of polyhydric alcohols per mole of propiolaldehyde was (in g): for methyl homolog 12, ethyl 21, propyl 32, butyl 37 and isobutyl 20.

The diacetylenic glycol with a propyl radical

$$HC\equiv C-CH(OH)-C\equiv C-CH(OH)-C_3H_7-$$

was a viscous liquid. Its yield was about 80% of the corresponding higher fraction.

B.p. 130° (3 mm), 144° (6 mm), d_4^{20} 1.0300, n_D^{20} 1.4942, MR 43.03. $C_9H_{12}O_2$. Calculated 42.81. 18.04 mg substance: 46.89 mg CO_2; 13.82 mg H_2O. 0.1050, 0.2369 g substance; 16.9 g CH_3COOH: Δt 0.162°, 0.352°. 0.0920 g substance: 44.9 ml CH_4 (26°, 753 mm). Found %: C 70.93; H 7.57. M 149.6, 155.3. Active H 3.0. $C_9H_{12}O_2$. Calculated %: C 71.03; H 7.95. M 152. Active H 3.0.

TABLE 5

Substance	Weight of sample (g)	Weight of AgBr (g)	Br (%) Found	Br (%) Calculated
CHBr=CBr – CH (OH) –CH_3	0.1454	0.2368	69.31	69.51
CHBr=CBr – CH (OH) – C_2H_5	0.2536	0.3912	65.64	65.52
CHBr=CBr – CH (OH) – C_3H_7	0.1493	0.2181	62.17	61.96
CHBr=CBr – CH (OH) – C_4H_9	0.1601	0.2211	58.77	58.76

Hydrogenation was carried out with 0.6443 g glycol, 35 ml methyl alcohol and 3 ml colloidal palladium with a metal content of 1.53 mg per ml. The experiment was performed at 28° and 754 mm. The calculated amount of hydrogen was 421.6 ml. 416 ml was absorbed or 98.7%. Hydrogen was measured at intervals of 1, 3, 15 and then 60 minutes. The course of the hydrogenation is characterized by the shortened Table 6.

TABLE 6

Duration (in minutes)	3	6	9	12	15	30	45	60	120	180	240	300	360	480	1080	1440
Found H absorbed (mole-%)	9.5	15.4	20.6	25.8	30.8	47.9	56.4	61.4	71.1	76.1	78.8	83.3	86.5	89.4	96.9	98.7

SUMMARY

1. The reaction of propiolaldehyde with organomagnesium compounds was investigated, and it was shown that the main reaction products are alkylpropargyl alcohols and diacetylenic glycols.

2. Some uninvestigated alkylpropargyl alcohols and their acetates and dibromides were described.

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Leningrad Lensovet Institute of Technology and Friedrich Schiller University, Jena

TERTIARY TRIHYDRIC ALCOHOLS OF THE ACETYLENIC SERIES AND THEIR TRANSFORMATIONS

VI. SYNTHESIS OF 2,3,6-TRIMETHYLOCTYN-4-TRIOL-2,3,6; TRIMETHYLNONYN-5-TRIOL-3,4,7; 2-METHYL-5-(1-HYDROXYCYCLOPENTYL)-HEXYN-3-DIOL-2,5, AND 2,4-DI-(1-HYDROXYCYCLOPENTYL)-BUTYN-3-OL-2

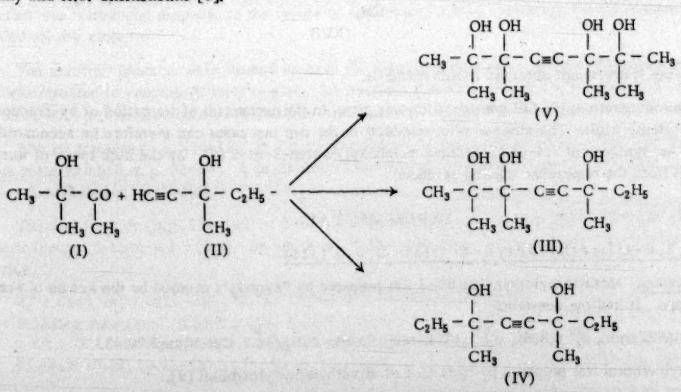
V.I. Nikitin and S.D. Savranskaya

In previous communications [1,2] a method was given for preparation of tertiary trihydric alcohols of the acetylenic series. Recently a paper was published in a French journal by Colonge and Clerc [3] which describes the preparation of triols of the acetylenic series, both tertiary and primary-tertiary. These authors write that they failed to isolate a single acetylenic triol because of decomposition when distilled even in high vacuum. We consider it necessary to declare that this statement is untrue in respect of tertiary glycerols of the acetylenic series. On the contrary, such glycerols exhibit exceptional stability. They are very easily distilled in vacuum and can be stored completely unchanged over many years.

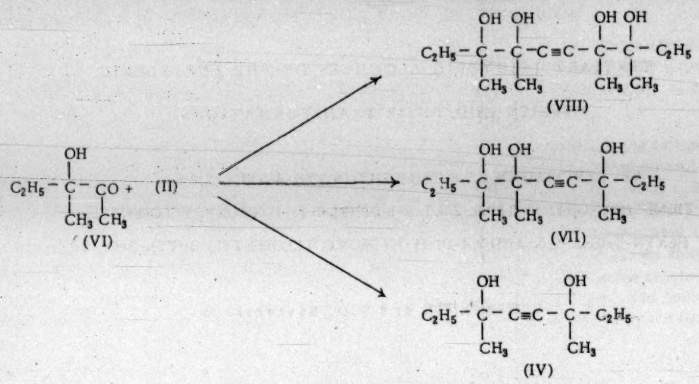
We have isolated a sufficiently large number of various representatives of this class of compounds. In particular, 2,3,6-trimethylheptyn-4-triol-2,3,6, which Colonge and Clerc did not isolate in the pure form and which they describe only as the product of its exhaustive hydrogenation, was obtained many times and had already been described by one of us in 1945 [1,4].

In the present paper we report the synthesis of four new representatives of the alcohols of this series.

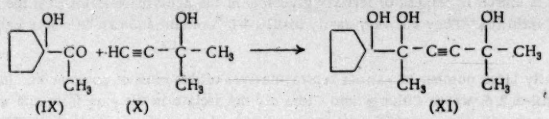
Condensation of dimethylacetylcarbinol (I) with methylethylethynylcarbinol (II) gave 2,3,6-trimethyloctyn-4-triol-2,3,6 (III) with b.p. 121-122° (1.5 mm), an isomer of the 3,4,7-trimethyl-octyn-5-triol-3,4,7 previously described by us. By-products were asymm. γ-glycol-dimethyldiethylbutynediol (IV) – and an asythritol – 2,3,6,7-tetramethyloctyn-4-tetraol-2,3,6,7 (V) – with m.p. 154-155°, which had previously been synthesized by A.E. Favorsky and A.S. Onishchenko [5].



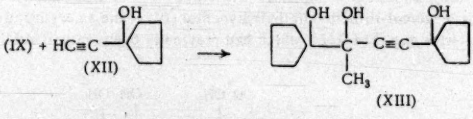
Condensation of methylethylacetylcarbinol (VI) with methylethylethynylcarbinol (II) gave 3,4,7-trimethylnonyn-5-triol-3,4,7 (VII) in a yield of 80-83% in the form of a viscous liquid with b.p. 124-126° (2 mm); by-products isolated in this process are symm. dimethyldiethylbutynediol (IV) and an acetylenic erythritol— 3,4,7,8-tetramethyldecyn-5-tetraol-3,4,7,8 (VIII)— which was obtained for the first time by Onishchenko [6].



Condensation of 1-acetylcyclopentanol (IX) with dimethylethynylcarbinol (X) led to 2-methyl-5-(1-hydroxycyclopentyl)-hexyn-3-diol-2,5 (XI) – a vitreous substance crystallizing from benzene or aqueous alcohol with two molecules of water with m.p. 68-69°. Yield 72%. No by-products were isolated.



Condensation of acetylcyclopentanol (IX) with 1-ethynylcyclopentanol (XII) gave an acetylenic glycerol with two cyclopentyl rings – 2,4-(1-hydroxycyclopentyl)-butyn-3-ol-2 (XIII) – with b.p. 168-170° (2.5 mm). It crystallizes from benzene with two molecules of water, m.p. 93-94°. The yield of triol is 74% of the acetylcyclopentanol taken into reaction.



By-products were likewise not obtained in this synthesis.

In previous communications [2] full consideration was given to the mechanism of formation of by-products during synthesis of acetylenic triols. The absence of by-products in the two last cases can therefore be accounted for in the same way as in the synthesis of 2,4-di-(1-hydroxycyclohexyl)-butyn-3-ol-2 [2]: by the high speed of formation of these stable triols from the respective starting products.

EXPERIMENTAL

Synthesis of 2,3,6-trimethyloctyn-4-triol-2,3,6 (III)

Starting substances. Methylethylethynylcarbinol was prepared by Favorsky's method by the action of acetylene on methylethyl ketone. It had the constants:

B.p. 117-119° (692 mm), d_4^{20} 0.8692, n_D^{20} 1.4311, MR_D 29.18. $C_6H_{10}O$. Calculated 29.43.

Dimethylacetylcarbinol was prepared by hydration of dimethylethynylcarbinol [9].

B.p. 135-137° (689 mm), d_4^{20} 0.9518, n_D^{20} 1.4160, MR_D 26.88. $C_5H_{10}O_2$. Calculated 26.82.

A mixture of 24 g (0.25 mole) methylethylethynylcarbinol and 26 g (0.25 mole) dimethylacetylcarbinol in 150 ml dry ether was introduced dropwise over a period of 4 hours into a flask fitted with a mechanical stirrer containing 30 g powdered potassium hydroxide in 500 ml dry ether. The flask was immersed in an ice bath with

temperature of −2 to −3°. With progressive addition of the mixture to the reaction flask, the contents of the latter thickened to a light-yellow mass. The next day the resultant complex was decomposed with a small quantity of water (60 ml), the ether layer was separated from the aqueous alkaline layer, and the latter was extracted several times with ether. The ethereal layer, combined with the extracts, was washed with 5% hydrochloric acid and dried, and the ether was driven off. Weight of crude product 45.4 g. Unreacted starting components were first distilled off (8.1 g), and the residue was subjected to distillation in vacuum at 2 mm to give the following fractions: 1st fraction, b.p. 90-120°, 4.3 g; 2nd fraction, b.p. 120-126°, 30.8 g (a viscous liquid); 3rd fraction, b.p. 126-140°, 2.6 g (crystallized).

The 1st fraction (b.p. 90-120° at 2 mm) crystallized. After pressing on a porous plate, the crystals melted at 52-53°. A mixed sample with dimethyldiethylbutynediol (IV) did not show a melting point depression (according to the literature the m.p. is 54° [7]).

The 2nd fraction (b.p. 120-126° at 2 mm) was distilled in vacuum. It was a viscous liquid, 2,3,6-trimethyloctyn-4-triol-2,3,6 (III). Its yield on the ketoalcohol taken in the reaction was 60%.

B.p. 121-122° (1.5 mm), d_4^{20} 1.0215, n_D^{20} 1.4799, MR_D 55.60. $C_{11}H_{20}O_3$ F. Calculated MR_D 55.57.

This fraction crystallized on standing. Recrystallization from ligroine gave red prisms with m.p. 57-59°.

0.1819 g sub.: 0.4423 g CO_2; 0.1671 g H_2O. 0.1192 g sub.: 0.2878 g CO_2; 0.1072 g H_2O. 0.1006 g sub.: 39.2 ml CH_4 (21°, 688.8 mm). 0.0850 g sub.: 34.0 ml CH_4 (20°, 692.1 mm). Found %: C 66.29, 65.85; H 10.28, 10.06; OH 24.96, 25.81. $C_{11}H_{20}O_3$. Calculated %: C 66.00; H 10.00; OH 25.51.

Decomposition of 4 g of the substance with m.p. 57-59° by heating with potassium carbonate (0.3 g) [7] led to evolution of acetylene (test with ammoniacal silver oxide and cuprous chloride), and methylethyl ketone (semicarbazone m.p. 146-147°) and dimethylacetylcarbinol semicarbazone m.p. 160-161°) were isolated.

The 3rd fraction (b.p. 126-140° at 2 mm) melted at 154-155° after several recrystallizations from acetone and was the erythritol: 2,3,6,7-tetramethyloctyn-4-tetraol-2,3,6,7 (V) which was first described by Favorsky and Onishchenko. We identified it by a mixed test with an authentic specimen; the melting point remained unchanged.

Synthesis of 3,4,7-trimethylnonyn-5-triol-3,4,7 (VII)

Starting substances. Methylethylethynylcarbinol was prepared as indicated for the preceding synthesis and had the same constants. Methylethylacetylcarbinol was prepared from methylethylethynylcarbinol by hydration (Kucherov's method).

B.p. 148-149°, d_4^{20} 0.9386, n_D^{20} 1.4220, MR_D 31.43. $C_6H_{12}O_2$. Calculated 31.45.

A mixture of 30 g methylethylethynylcarbinol and 25 g methylethylacetylcarbinol (0.25 mole each) in 150 ml dry ether was introduced dropwise in the course of 4 hours into a flask containing 30 g powdered potassium hydroxide and 500 ml dry ether.

The reaction products were worked up as in the preceding synthesis. Weight of crude product 55 g. The product was distilled in vacuum (3 mm) to give: 1st fraction, b.p. 105-135°, 3.1 g (crystallized); 2nd fraction, b.p. 135-140°, 38.4 g (viscous liquid); 3rd fraction, b.p. 140-160°, 4.7 g (crystals). Residue in flask 2.4 g.

The 1st fraction (b.p. 105-135° at 3 mm) was dimethylethylbutynediol (IV). The crystals were pressed on a porous plate and had m.p. 52-53°. A depression of melting point did not occur in a test on a mixture with authentic symm. dimethylethylbutynediol.

The 2nd fraction (b.p. 135-140° at 3 mm) distilled over almost completely at 124-126° (2 mm) and was 3,4,7-trimethylnonyn-5-triol-3,4,7 (VII). Its yield was 83.5% calculated on the methylethylacetylcarbinol taken in the reaction.

d_4^{20} 1.0143, n_D^{20} 1.4810, MR_D 60.03. $C_{12}H_{22}O_3$ F. Calculated 60.18.
0.1441 g substance: 0.3560 g CO_2; 0.1338 g H_2O. 0.2028 g substance: 0.4992 g CO_2; 0.1887 g H_2O. 0.0760 g sub.: 28.4 ml CH_4 (29°, 682.9 mm). 0.0682 g sub.: 26.4 ml CH_4 (30.5°, 682.9 mm). Found %: C 67.32, 67.23; H 10.38, 10.41; OH 23.10, 23.80. $C_{12}H_{22}O_3$. Calculated %: C 67.29; H 10.28; OH 23.83.

On heating 6 g substance with m.p. 124-126° (2mm) with potassium carbonate (0.3 g), methylethyl ketone (2-4-dinitrophenylhydrazone, m.p. 114-115°) and methylethylacetylcarbinol (2,4-dinitrophenylhydrazone, m.p. 107-108°) were obtained.

The 3rd fraction (b.p. 140-160° at 3 mm) was recrystallized several times from acetone. The crystals melted at 155-156° and consisted of the erythritol: 3,4,7,8-tetramethyldecyn-5-tetraol-3,4,7,8 (VIII), first described by

Onishchenko [6]. The erythritol was identified from the melting point of its mixture with an authentic specimen.

Synthesis of 2-methyl-5-(1-hydroxycyclopentyl)-hexyn-3-diol-2,5 (XI)

Starting substances. Dimethylethynylcarbinol was prepared by the action of acetylene on acetone (Favorsky's method).

B.p. 99-101° (696 mm), d_4^{20} 0.8614, n_D^{20} 1.4204, MR_D 24.70. C_5H_8O F. Calculated 24.81.

Acetylcyclopentanol was prepared by hydration of ethynylcyclopentanol obtained by Favorsky's method under conditions suggested by I.A. Favorskaya and L.V. Fedorova [8], and had the following constants:

B.p. 70-71° (8mm), d_4^{20} 1.0437, n_D^{20} 1.4674, MR_D 34.04. $C_7H_{12}O_2$. Calculated 33.86.

A mixture of 30 g dimethylethynylcarbinol and 32 g acetylcyclopentanol (0.25 mole each) in 150 ml dry ether was introduced dropwise over a period of 6 hours into a flask containing 30 g powered potassium hydroxide in 600 ml dry ether. The subsequent operations were similar to those in the previous synthesis.

The product was fractionated in vacuum (3 mm), the following fractions being collected: 1st fraction, b.p. up to 142°, 13.6 g, n_D^{20} 1.4670; 2nd fraction, b.p. 142-158°, 38.2 g; residue 2 g. Yield of main product (XI) 72.3% reckoned on the acetylcyclopentanol taken in the reaction.

The 1st fraction was a mixture of unreacted starting substances, mainly acetylcyclopentanol.

The 2nd fraction was a glassy, solid substance. On redistillation in vacuum at 3 mm it boiled at 150-151°.

0.1362 g substance: 0.3362 g CO_2; 0.1144 g H_2O. 0.1228 g substance: 0.3047 g CO_2; 0.1077 g H_2O. 0.0648 g substance: 23.4 ml CH_4 (21°, 695.5 mm). 0.0786 g substance: 30.2 ml CH_4 (23°, 697.2 mm). Found %: C 67.33; 67.66; H 9.40, 9.81; OH 23.34, 24.98. $C_{12}H_{20}O_3$. Calculated %: C 67.92; H 9.43; OH 24.05.

The fraction with b.p. 150-151° (3 mm) crystallizes from benzene or aqueous ethyl alcohol. The crystals in the air-dry state melt at 68-69° and consist of 2-methyl-5-(1-hydroxycyclopentyl)-hexyn-3-diol-2,5 (XI), which crystallizes with two molecules of water.

0.1236 g substance: 0.2637 g CO_2; 0.1094 g H_2O. 0.1063 g substance: 0.2252 g CO_2; 0.0949 g H_2O. 0.0666 g substance: 35.6 ml CH_4 (21.5°, 701.2 mm). 0.0613 g substance: 32.4 ml CH_4 (20°, 696.0 mm). Found %: C 58.19, 57.79; H 9.90, 9.99; active H 1.99, 2.03. $C_{12}H_{20}O_3 \cdot 2H_2O$. Calculated %: C 58.06; H 9.67; active H 2.02.

Scission of 4.8 g substance (m.p. 68-69°) by heating with potassium carbonate (0.3 g) gave acetylene, acetone (2,4-dinitrophenylhydrazone m.p. 124-125°) and acetylcyclopentanol (semicarbazone m.p. 188-189°).

No by-products were obtained in the synthesis. From the flask residue was isolated 0.5 g crystals which melted at 224-225° but could not be investigated due to the small amount.

Synthesis of 2,4-di-(1-hydroxycyclopentyl)-3-butyn-2-ol (XIII)

Starting substances. Ethynylcyclopentanol was prepared by the Favorsky reaction [8] and had the following constants:

B.p. 155-156° (686 mm) d_4^{20} 0.9737, n_D^{20} 1.4751, MR_D 31.31. $C_7H_{10}O$ F. Calculated 31.84.

Acetylcyclopentanol was prepared as in the previous synthesis and had the same constants.

A mixture of 35 g ethynylcyclopentanol and 32 g acetylcyclopentanol (0.25 mole each) in 150 ml dry ether was added dropwise in the course of 6 hours to a flask containing 45 g powdered potassium hydroxide in 600 ml dry ether. The reaction mixture was worked up in the usual way at the end of the reaction. Treatment of the ether solution with hydrochloric acid led to separation of 26.7 g crystals which after recrystallization from benzene melted at 93-94°. The product remaining after removal of the ether was vacuum-distilled and the following fractions were collected: 1st fraction b.p. to 168° (5-3.5 mm), 16.9 g, n_D^{20} 1.4750; 2nd fraction, b.p. 168-170° (2.5 mm), 17.6 g, a viscous liquid; flask residue 2.5 g.

The 1st fraction (b.p. to 168° at 5-3.5 mm) is unreacted starting substances.

The 2nd fraction (b.p. 168-170° at 2.5 mm) on recrystallization from benzene gives crystals melting at 93-94° and identical with the crystals coming down from the ether solution. They are 2,4-di(1-hydroxycyclopentyl)-butyn-3-ol-2 (XIII), crystallizing with two molecules of water. Yield about 73% on the acetylcyclopentanol taken in the reaction.

0.1266 g substance: 0.2832 g CO_2; 0.1096 g H_2O. 0.1362 g substance: 0.3036 g CO_2; 0.1168 g H_2O · 0.0665 g substance: 30.4 ml CH_4 (18.5°, 693.3 mm). 0.0619 g substance: 27.9 ml CH_4 (19.5°, 689.0 mm). Found %: C 60.99, 60.81; H 9.68, 9.60; active H 1.75, 1.71. $C_{14}H_{22}O_3 \cdot 2H_2O$. Calculated %: C 61.31; H 9.49; active H 1.82.

A weighed amount of 2.1572 g crystals (m.p. 93-94°) was kept in a vacuum desiccator at 50-60° until the weight was constant. The loss was 0.2616 g. Calculated for 2 molecules of water per 1 molecule of the triatomic alcohol 0.2400 g.

0.0928 g substance: 0.2408 g CO_2; 0.0804 g H_2O. 0.1156 g substance: 0.2976 g CO_2; 0.1008 g H_2O. 0.0838 g substance: 30.8 ml CH_4 (21.6°, 689.6 mm). Found %: C 70.76, 70.04; H 9.69, 9.75; OH 23.52. $C_{14}H_{22}O_3$. Calculated %: C 70.60; H 9.24; OH 21.42.

Heating of 5 g substance (m.p. 93-94°) with 0.4 g potassium carbonate gave acetylene, cyclopentanone (2,4,-dinitrophenylhydrazone, m.p. 144-145°) and acetylcyclopentanol (semicarbazone m.p. 188-189°).

By-products were again not detected in this synthesis.

SUMMARY

1. New representatives of the class of tertiary trihydric alcohols of the acetylenic series were obtained: 2,3,6-trimethyloctyn-4-triol-2,3,6; 3,4,7-trimethylnonyn-5-triol-3,4,7; 2-methyl-5-(1-hydroxycyclopentyl)-hexyn-3-diol-2,5; and 2,4-di-(1-hydroxycyclopentyl)-butyn-3-ol-2.

2. Corresponding by-products were obtained in the synthesis of trimethyloctynetriol and trimethylnonynetriol due to partial breakdown of the original acetylenic carbinol.

3. Acetylcyclopentanol condenses with acetylenic carbinols to form the corresponding tertiary acetylenic glycerols without formation of any by-products whatsoever.

4. Tertiary acetylenic glycerols containing cyclopentyl radicals differ from all other known acetylenic alcohols in crystallizing with two molecules of water.

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Institute of Chemistry, Academy of Sciences, Tadjik SSR

• T.p. = C.B. Translation paginations.

HYDRATION OF VINYLACETYLENIC HYDROCARBONS IN SOLUTIONS OF ALCOHOLS AND PHENOLS

I. N. Nazarov, S.A. Vartanyan and S.G. Matsoyan

It was previously shown that hydration of vinylacetylene and divinylacetylenic hydrocarbons in alcoholic solutions in presence of mercury sulfate readily leads to formation of the corresponding β-alkoxyketones [1].

The first stage of these reactions is the hydration of the triple bond with formation of unsaturated ketones which under the experimental conditions add on alcohols to give the corresponding β-alkoxyketones as the final products of hydration.

It was a matter of interest to explore the possibility of hydration of vinylacetylene in phenols. It was found that on passing vinylacetylene into aqueous solutions of phenol and of m-cresol in presence of mercury sulfate, methyl-β-phenoxyethyl ketone and methyl-β-m-cresoxyethyl ketone are formed in yields of 50 and 30% respectively.

$$CH_2 = CH - C \equiv CH \xrightarrow[HgSO_4]{H_2O,\ ArOH} ArOCH_2CH_2COCH_3.$$

$$Ar = C_6H_5,\ m\text{-}CH_3C_6H_4$$

In the present research we also studied the hydration of homologs of vinylacetylene in alcoholic solutions. As had been expected, isopropenylacetylene, similarly to vinyiacetylene, is hydrated in alcoholic solutions, forming methyl-β-alkoxyisopropyl ketones in a yield of up to 50%.

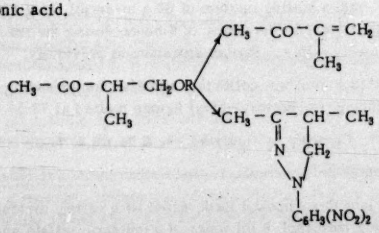
$$CH_2 = \underset{\underset{CH_3}{|}}{C} - C \equiv CH \xrightarrow[HgSO_4]{H_2O,\ ROH} ROCH_2 - \underset{\underset{CH_3}{|}}{CH} - CO - CH_3.$$

The hydration was realized by gradual introduction of isopropenylacetylene and water into a boiling aqueous alcoholic mixture containing mercury sulfate and sulfuric acid as catalyst. The water was added gradually to maintain the homogeneity of the reaction mixture. The yields of methyl-β-alkoxyisopropyl ketones increased with diminishing molecular weight of the alcohol. With secondary alcohols the yield of alkoxyketone was very much lower than with primary alcohols.

All the methyl-β-alkoxyisopropyl ketones that we prepared (see table) are colorless liquids with a fruity odor.

As we had previously shown [1], hydration of vinylacetylene in alcoholic solutions leads to very much higher yields of methyl-β-alkoxyethyl ketones. This indicates that methylvinyl ketone adds on alcohols with very much greater facility than methylisopropyl ketone.

The alcohols are split off with extraordinary ease when methyl-β-alkoxyisopropenyl ketones are distilled in presence of p-toluenesulfonic acid.



Quantitative formation of 3,4-dimethyl-N-(2,4-dinitrophenyl)-pyrazoline took place in all cases when an attempt was made to prepare the 2,4-dinitrophenylhydrazones of the above-listed β-alkoxyketones by the action of an acidified alcoholic solution of 2,4-dinitrophenylhydrazine.

It is interesting to note that more drastic conditions are required for the realization of this cyclization with methyl-β-alkoxyethyl ketones.

Preparation No.	Formula	Boiling point at pressure (mm)	n_D^{20}	n_4^{20}	Yield (%)
1	$CH_3OCH_2CH(CH_3)COCH_3$ (I)	140-141° (676)	1.4130	0.9070	50
2	$C_2H_5OCH_2CH(CH_3)COCH_3$ (II)	152-153 (680)	1.4140	0.8911	41
3	iso-$C_3H_7OCH_2CH(CH_3)COCH_3$ (III)	168-170 (678)	1.4205	0.8925	18.5
4	$C_3H_7OCH_2CH(CH_3)COCH_3$ (IV)	172-173 (670)	1.420	0.8888	34
5	iso-$C_4H_9OCH_2CH(CH_3)COCH_3$ (V)	183-184 (677)	1.4190	0.8723	30.5
6	$C_4H_9OCH_2CH(CH_3)COCH_3$ (VI)	191-193 (678)	1.4215	0.8775	32
7	iso-$C_5H_{11}OCH_2CH(CH_3)COCH_3$ (VII)	202-204 (677)	1.4250	0.8767	26.5
8	$C_6H_{11}OCH_2CH(CH_3)COCH_3$ (VIII)	84-85 (3)	1.4600	0.9678	11.3
9	$C_8H_{17}OCH_2CH(CH_3)COCH_3$ (IX)	120-121 (6)	1.4395	0.8882	22.5

Hydration of 3-methyl-2-penten-4-yne in alcoholic solutions already fails to give the corresponding alkoxy ketones; instead only 3-methyl-2-penten-4-one is formed in high yield; this illustrates the inability of disubstituted α,β-unsaturated ketones to add on alcohols.

$$CH_3-CH=C(CH_3)-C\equiv CH \xrightarrow[HgSO_4]{H_2O,\ ROH} CH_3-CH=C(CH_3)-CO-CH_3$$

EXPERIMENTAL

Methyl-β-phenoxyethyl ketone. A mixture of 80 g phenol, 20 g 10% sulfuric acid and 5 g mercury sulfate was placed in a three-necked flask fitted with a mechnical stirrer with a mercury seal, a condenser and a bubbler. Into the boiling reaction mixture with continuous stirring was introduced 30 g vinylacetylene in the course of 6 hours. During the hydration, 20 g water and an additional 5 g mercury sulfate were added. Stirring was then continued for 2 hours. The product was treated with aqueous sodium carbonate, extracted with ether, and dried with sodium sulfate.

After driving off the ether, the residue was distilled in vacuum and a 150-155° (3 mm) fraction was collected which crystallized on standing. After recrystallization from gasoline-ethanol mixture, 47 g methyl-β-phenoxyethyl ketone was obtained with m.p. 80-81°.

Found %: C 73.07, 73.42; H 7.62, 7.66. $C_{10}H_{12}O_2$. Calculated %: C 73.14; H 7.31.

The 2,4-dinitrophenylhydrazone was prepared by the action of a hot, acidified alcoholic solution of 2,4-dinitrophenylhydrazine on an alcoholic solution of methyl-β-phenoxyethyl ketone; m.p. 141-145° (from ethanol).

Methyl-β-(m-cresoxy)-ethyl ketone. Into a boiling mixture of 60 g m-cresol, 10 g 10% sulfuric acid and 3 g mercuric sulfate was introduced 32 g vinylacetylene in the course of 6 hours; during the reaction further addition was made portionwise of 10 g water and 5 g mercury sulfate. Further procedure as previously.

32.5 g of a fraction with b.p. 162-169° (2.5 mm) was collected, and after long standing it crystallized. After recrystallization from ethanol-benzene, methyl-β-(m-cresoxy)-ethyl ketone melted at 73-74,5°.

Found %: C 74.61, 74.60; H 8.27, 8.37. $C_{11}H_{14}O_2$. Calculated %: C 74.13; H 7.92.

The 2,4-dinitrophenylhydrazone of methyl-β-(m-cresoxy)-ethyl ketone melted at 178-180° (from ethanol).

Methyl-β-methoxyisopropyl ketone. In a three-necked flask, fitted with stirrer, mercury seal, condenser, dropping funnel and thermometer, were put 110 g methanol, 6 ml water, 3 g mercuric sulfate and 2 ml conc. sulfuric acid. In the course of 5 hours addition was made dropwise to the boiling mixture, with stirring, of a solution of 37 g isopropenylacetylene [2] in 57 g methanol; at the same time 14 g water and 10 g mercuric sulfate were introduced into the reaction mixture in small portions. The stirring was subsequently continued for 4 hours. The main bulk of the methanol was distilled off in a low vacuum on a water bath. The residue was neutralized with aqueous potassium carbonate solution and extracted with ether. The ethereal extract was dried with sodium sulfate, and the product (after removal of the ether)

distilled, at first in vacuum and later at atmospheric pressure. Yield 32 g methyl-β-methoxyisopropyl ketone.

B.p. 52-53° (22 mm), 140-141° (676 mm), n_D^{20} 1.4130, d_4^{20} 0.9070. MR 31.95; Calculated 31.56.
Found %: C 62.06, 62.24; H 10.22, 10.32. $C_6H_{12}O_2$. Calculated %: C 62.07; H 10.34.

Methyl-β-ethoxyisopropyl ketone. To a boiling mixture of 95 g ethanol, 5 ml water, 1 ml conc. sulfuric acid, and 1.5 g mercuric sulfate was added dropwise over a period of 6 hours a solution of 30 g isopropenylacetylene in 40 ml ethanol; at the same time portionwise addition was made of 20 g water and 8 g mercuric sulfate. Stirring was afterwards continued for 3 hours at 70-75°. Further treatment was as described above.

24 g methyl-β-ethoxyisopropyl ketone was obtained.

B.p. 70-71° (33 mm), 152-153° (680 mm), n_D^{20} 1.4140, d_4^{20} 0.8911, MR 36.52; Calculated 36.19.
Found %: C 64.97, 65.06; H 10.95, 10.73. $C_7H_{14}O_2$. Calculated %: C 64.53; H 10.83.

Methyl-β-isopropoxyisopropyl ketone. A mixture of 60 g isopropyl alcohol, 3 ml water, 1 ml conc. sulfuric acid, 3 g mercuric sulfate and 33 g isopropenyl acetate was heated for 5 hours. In the course of the hydration 20 g water and 7 g mercuric sulfate were added. Further treatment as above. 13.3 g methyl-β-isopropoxyisopropyl ketone was obtained.

B.p. 168-170° (678 mm), n_D^{20} 1.4205, d_4^{20} 0.8925, MR 40.90, Calculated: 40.80.
Found %: C 66.24, 66.45; H 11.53, 11.24. $C_8H_{16}O_2$. Calculated %: C 66.66; H 11.11.

Methyl-β-propoxyisopropyl ketone. To a boiling mixture of 80 g propyl alcohol, 3 ml water, 2 ml conc. sulfuric acid and 1.5 g mercuric sulfate was added a solution of 24 g isopropenylacetylene in 30 g propyl alcohol in the course of 6 hours; at the same time portionwise addition was made of 15 g water and 4 g mercuric sulfate. Stirring was then continued for 3 hours at 80°.

The product was worked up in the usual way. Yield 17.7 g methyl-β-propoxyisopropyl ketone.

B.p. 67-68° (14 mm), 172-173° (680 mm), n_D^{20} 1.4200, d_4^{20} 0.8888, MR 41.1; Calculated 40.8.
Found %: C 66.16, 65.82; H 11.52, 11.11. $C_8H_{16}O_2$. Calculated %: C 66.66; H 11.11.

Methyl-β-isobutoxyisopropyl ketone. To a heated mixture (100°) of 100 g isobutyl alcohol, 3 ml water and 1 g mercuric sulfate was added a solution of 26 g isopropenylacetylene in 30 g isobutyl alcohol over a period of 6 hours. During the same period 25 ml water and 6 g mercuric sulfate were introduced into the reaction mixture. Yield 19 g methyl-β-isobutoxyisopropyl ketone.

B.p. 67-68° (10 mm), 183-184° (677 mm), n_D^{20} 1.4190, d_4^{20} 0.8723, MR 45.80; Calculated: 45.41.
Found %: C 68.18, 68.26; H 11.51, 11.54. $C_9H_{18}O_2$. Calculated %: C 68.32; H 11.47.

Methyl-β-butoxyisopropyl ketone. To a boiling mixture of 100 g butyl alcohol, 2 ml conc. sulfuric acid, 10 ml water and 2 g mercuric sulfate was added dropwise a solution of 60 g isopropenylacetylene in 90 g butyl alcohol in the course of 10 hours, while 30 g water and 13 g mercuric sulfate were additionally introduced. Yield 46 g methyl-β-butoxyisopropyl ketone.

B.p. 74-75° (10 mm), 191-193° (678 mm), n_D^{20} 1.4215, d_4^{20} 0.8773, MR 45.75; Calculated: 45.41.
Found %: C 68.67, 68.77; H 11.49, 11.80. $C_9H_{18}O_2$. Calculated %: C 68.32; H 11.47.

Methyl-β-isoamyloxyisopropyl ketone. To a boiling mixture of 100 g isoamyl alcohol, 10 g water, 3 ml conc. sulfuric acid and 2 g mercuric sulfate was added a solution of 35 g isopropenylacetylene in 50 g isoamyl alcohol in the course of 7 hours. During this period a further 15 g water and 10 g mercuric sulfate were added. Yield 24.2 g methyl-β-isoamyloxyisopropyl ketone.

B.p. 202-204° (677 mm), 64-65° (3.5 mm), n_D^{20} 1.425, d_4^{20} 0.8767, MR 50.48; Calculated: 50.03.
Found %: C 69.33, 69.17; H 11.79, 11.60. $C_{10}H_{20}O_2$. Calculated %: C 69.72; H 11.70.

Methyl-β-cyclohexoxyisopropyl ketone. To a heated mixture (90°) of 100 g cyclohexanol, 5 ml water, 2 g mercuric sulfate and 1 ml conc. sulfuric acid was added a solution of 33 g isopropenylacetylene in 40 g cyclohexanol in the course of 7 hours. Simultaneously 30 g water and 8 g mercuric sulfate were added to the reaction mixture. Yield 10.4 g methyl-β-cyclohexoxyisopropyl ketone.

B.p. 84-85° (3 mm), n_D^{20} 1.4600, d_4^{20} 0.9678, MR 52.13; Calculated 52.44.
Found %: C 71.50, 71.45; H 10.97, 10.90. $C_{11}H_{20}O_2$. Calculated %: C 71.69; H 10.94.

Methyl-β-octyloxyisopropyl ketone. To a heated mixture (95-100°) of 64 g octyl alcohol, 2 ml water, 2 ml conc. sulfuric acid and 3 g mercuric sulfate was added a solution of 30 g isopropenylacetylene in 26 g octyl alcohol in the course of 6 hours, while 20 ml water and 8 g mercuric sulfate were additionally introduced into the reaction mixture. Yield 22 g methyl-β-octyloxyisopropyl ketone.

B.p. 120-121° (6 mm), n_D^{20} 1.4395, d_4^{20} 0.8882, MR 63.22, Calculated 63.81.
Found %: C 72.70, 72.88; H 11.78, 11.60. $C_{13}H_{26}O_2$. Calculated %: C 72.88; H 12.23.

Detachment of alcohols from methyl-β-alkoxyisopropyl ketones. A mixture of 10 g methyl-β-methoxyisopropyl ketone and 0.1 g p-toluenesulfonic acid was heated in a Wurtz flask at 100° for 20 minutes. Toward the end of the

distillation the bath temperature was raised to 120°. 9.2 g of cleavage products with b.p. 60-100° was collected. Redistillation gave 6.9 g methylisopropenyl ketone [3] with b.p. 93-96°, n_D^{20} 1.4217.

Reaction of an acidified alcoholic solution of 2,4-dinitrophenylhydrazine with methylisopropenyl ketone gave 3,4-dimethyl-N-(2,4-dinitrophenyl)-pyrazoline with m.p. 190-191° (from methanol) [4]. Cleavage of other methyl-β-alkoxyisopropyl ketones was effected in a similar manner.

Action of 2,4-dinitrophenylhydazine upon methyl-β-alkoxyisopropyl ketones. To 3 g methyl-β-methoxyisopropyl ketone was added a hot acidified alcoholic solution of 2,4-dinitrophenylhydrazine (5.5 g). The next day the voluminous precipitate was washed with hot alcohol and dried. Yield 6.1 g 3,4-dimethyl-N(2,4-dinitrophenyl)-pyrazoline with m.p. 190-191°, not giving a depression of melting point with the above-described sample.

Found %: N 21.09, 21.29. $C_{11}H_{12}O_4N_4$. Calculated %: N 21.21.

The same results were obtained by the action of 2,4-dinitrophenylhydrazine upon methyl-β-isopropoxyisopropyl ketone and methyl-β-cyclohexoxyisopropyl ketone.

Hydration of 3-methyl-2-penten-4-yne in methanol. To a boiling mixture of 25 g methanol, 1 ml water, 1 ml conc. sulfuric acid and 1 g mercuric sulfate was added a solution of 7 g 3-methyl-2-penten-4-yne [5] in 15 ml methanol in the course of 2 hours. During this period 6 g water and 3 g mercuric sulfate were introduced into the reaction mixture. The stirring of the reaction mixture was thereupon continued for another 1 ½ hours. The methanol was taken off and the residue neutralized with 20% sodium carbonate solution and extracted with ether. The product was distilled, at first in vacuum and later at atmospheric pressure, to give 6.2 g 3-methyl-2-penten-4-one with b.p. 134-138° (680 mm), n_D^{20} 1.4395.

The semicarbazone comes down immediately on treatment with a saturated aqueous solution of semicarbazide hydrochloride and sodium acetate, m.p. 186-188° (from ethanol) [6].

Hydration of 3-methyl-2-penten-4-yne in propyl alcohol likewise led to 3-methyl-2-penten-4-one with b.p. 135-138° (680 mm).

SUMMARY

1. Hydration of vinylacetylene in aqueous solutions of phenols in presence of mercuric sulfate gives the corresponding methyl-β-aryloxyethyl ketones in about 50% yield.

2. Hydration of isopropenylacetylene in alcoholic solutions in presence of mercuric sulfate gives methyl-β-alkoxyisopropyl ketones in a yield of up to 50%. Yields of the latter were slightly lower than the yields of methyl-β-alkoxymethyl ketones formed by hydration of vinylacetylene in alcoholic solutions.

3. The alkoxy group in methyl-β-alkoxyisopropyl ketones is split off more easily than the one in β-alkoxyethyl ketones.

4. Hydration of 3-methyl-2-penten-4-yne in alcoholic solutions in presence of mercuric sulfate leads to formation of 3-methyl-2-penten-4-one alone in high yield.

5. Methylisopropenyl ketone adds on alcohols with considerably greater difficulty than methylvinyl ketone, while 3-methyl-2-penten-4-one is quite incapable of adding on alcohols.

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Chemistry Institute of the Academy of Sciences, Armenian SSR

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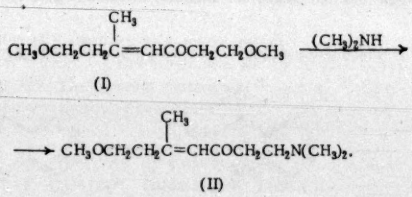
THE ACTION OF AMMONIA AND PRIMARY AMINES ON ALKOXY KETONES

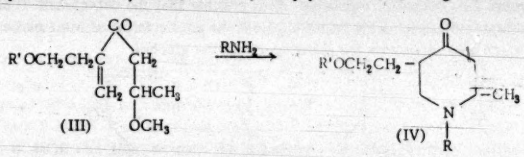
I.N. Nazarov, S.A. Vartanyan and V.N. Zhamagortsyan

Previous work in our laboratories showed that reaction of primary amines with β-alkoxy ketones readily leads to 4-piperidones [1]. Reaction of secondary amines with β-alkoxy ketones leads to formation of β-dialkylamino ketones [2]. In these reactions only those alkoxy groups proved to be reactive which are in the β-position to the carbonyl group. Thus, for instance, on heating a mixture of an aqueous solution of dimethylamine and 2-methyl-2-methoxybutan-3-one for 6 hours on a boiling water bath, the α-methoxy ketone is completely recovered, whereas β-alkoxy ketones readily enter into reaction with amines even at 50-60°.

Reaction of an aqueous solution of dimethylamine with 1,7-dimethoxy-3-methyl-3-hepten-5-one (I) results in aminolysis of only one β-methoxy group, 1-methoxy-3-methyl-7-dimethylamino-3-hepten-5-one (II) being formed in high yield.



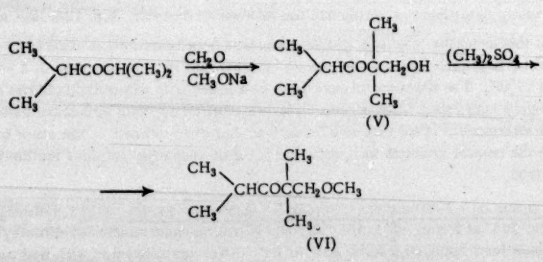
In the action of β, γ-dialkoxy ketones (III) of aqueous solutions of ammonia and primary amines, only the β-methoxy group again is split off, 2-methyl-5-β-alkoxethyl-4-piperidone (IV) being obtained in a yield of up to 70%.



R = H, CH_3, C_2H_5; R' = CH_3, C_2H_5, C_4H_9

The reaction of β-alkoxy ketones with ammonia and amines can proceed by two routes: by direct aminolysis or by splitting-off of alcohols followed by addition of the amines to the α,β-unsaturated ketones.

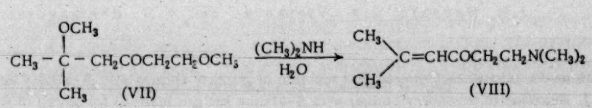
For the purpose of establishing the actual route, we investigated the reaction of secondary amines with 2,4,4-trimethyl-5-methoxypentan-3-one (VI), obtained by condensation of diisopropyl ketone with formaldehyde followed by methylation of the resultant ketoalcohol (V).



It was found that the methoxy ketone (VI) does not enter into reaction at all when heated with an aqueous solution of dimethylamine, or when heated with anhydrous piperidine for 6 hours on a boiling water bath; it is completely re-

covered unchanged. Consequently β-alkoxy ketones are capable of reacting with amines only on condition that hydrogen atoms are in the α-position to the carbonyl. We had previously established the removal of alcohols from β-alkoxy ketones under the action of amines [2].

A similar reaction is also described in the present paper in connection with 5-methyl-1,5-dimethoxyhexan-3-one (VII).

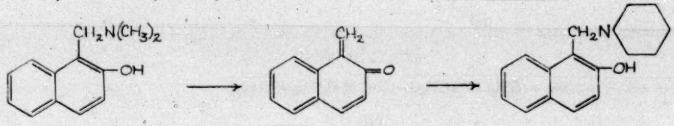


On stirring an aqueous solution of dimethylamine with the dimethoxy ketone (VII) and leaving the mixture to stand for 2 days at room temperature, the unsaturated aminoketone (VIII), previously described by us [2], is formed in 36% yield.

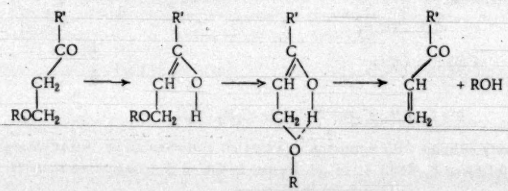
The experimental data show that β-alkoxy ketones enter into reaction with amines through splitting-off of alcohols with formation of α,β-unsaturated ketones which then add on the amines to give the corresponding β-aminoketones.

The amino exchange reaction of β-dialkylamino ketones likewise proceeds via removal of secondary amines with formation of α,β-unsaturated ketones which then add on another secondary amine and give new β-dialkylamino ketones [3].

Similarly, α-dimethylaminomethyl-β-naphthol enters into reaction with piperidine to give α-N-piperidyl-β-naphthol [4].



In the case of the methyl ether of this aminophenol, the amino exchange reaction does not take place [5], since detachment of dimethylamine then becomes impossible. It is possible that the detachment of alcohols from β-alkoxy ketones is associated with their enolization with formation from the enolic forms of intermediate cyclic compounds due to hydrogen bonding, which also facilitates the splitting-off of the alcohol.



EXPERIMENTAL

Action of dimethylamine on 2-methyl-2-methoxybutan-3-one. The methyl ether of dimethylacetylcarbinol, synthesized by the previously described method [6], had the following constants: b.p. 124-126° at 670 mm, n_D^{20} 1.4096.

A mixture of 9 g of this α-methoxy ketone and 25 g aqueous dimethylamine solution (24%) was heated in a glass ampoule on a boiling water bath for 6 hours. The excess of dimethylamine was removed in a vacuum of 50 mm while heating on a water bath to 40°. The reaction mixture was neutralized with dilute hydrochloric acid and the neutral products extracted throughly with ether. The organic bases were salted out with potassium carbonate and extracted with ether; the ethereal solution was dried with sodium sulfate, but after removal of the ether only about 0.5 g substance remained. From the neutral products was recovered 8.1 g of unchanged original methoxy ketone with b.p. 124-126° at 670 mm, n_D^{20} 1.4100.

Action of dimethylamine on 1,7-dimethoxy-3-methyl-3-hepten-5-one (I). 20 g 1,7-dimethoxy-3-methyl-3-hepten-5-one (I) (b.p. 98-105° at 2 mm, n_D^{20} 1.464 [10]) and 50 ml aqueous solution of dimethylamine (25%) were heated in a sealed ampoule for 2 hours on a water bath at 65°. After neutralization with hydrochloric acid and removal of the neutral products, the organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and distilled in vacuum to give 12.5 g 1-methoxy-3-methyl-7-dimethylamino-3-hepten-5-one (II).

B.p. 98-99° at 4 mm, n_D^{20} 1.476, d_4^{20} 0.9453, MR_D 59.39; calculated 58.13.
Found %: C 66.55, 66.41; H 10.90, 10.56. $C_{11}H_{21}O_2N$. Calculated %: C 66.33; H 10.56.

The hydrochloride of the prepared amino ketone (II) melts at 149-150° (from alcohol).

From the neutral products was obtained 2 g original 1,7-dimethoxy-3-methyl-3-hepten-5-one (I) with b.p. 95-103° at 3 mm, n_D^{20} 1.4630 [10].

Action of methylamine on 5-methoxy-2-β-methoxyethyl-1-hexen-3-one (III, R' = CH_3). A mixture of 20 g dimethoxy ketone (III, R' = CH_3)(b.p. 90-91° at 1 mm, n_D^{20} 1.4583 [10]), 20 g 30% aqueous solution of methylamine, and a small quantity of pyrogallol was heated in a sealed ampoule on a water bath at 65° for 2 hours. The reaction products were worked up in the usual way (see preceding experiment) to give 13.4 g of 1,2-dimethyl-3-β-methoxyethyl-4-piperidone (IV, R = R' = CH_3) in the form of a transparent, mobile liquid turning yellow on standing.

B.p. 99.5-102.5 at 3 mm, n_D^{20} 1.4715, d_4^{20} 0.9882, MR_D 52.43; calculated 51.77.
Found %: N 7.95, 7.94; OCH_3 18.56, 18.08 (Zeisel method). $C_{10}H_{19}O_2N$. Calculated %: N 7.57; OCH_3 16.75.

The 2,4-dinitrophenylhydrazone of the piperidone (IV, R = R' = CH_3) melts at 170° (from acetone); the hydrochloride melts at 165° (from alcohol).

From the neutral products was recovered 2.7 g of the original methoxy ketone with b.p. 106-108° at 8 mm, n_D^{20} 1.4670.

Action of ethylamine of 5-methoxy-2-β-methoxyethyl-1-hexen-3-one (III, R' = CH_3). A mixture of 14.2 g dimethoxy ketone (III, R' = CH_3), 9 g 50% ethylamine and 10 ml ethyl alcohol in a sealed ampoule was heated 6 hours on a water bath at 70°. The reaction mixture was worked up as in the preceding experiments to give 6.4 g 2-methyl-1-ethyl-5-β-methoxyethyl-4-piperidone (IV, R = C_2H_5, R' = CH_3) in the form of a yellowish, mobile liquid which darkens on standing.

B.p. 103-105° at 4 mm, n_D^{20} 1.4742, d_4^{20} 0.9752, MR_D 57.36; calculated 56.39.
Found %: N 7.04, 7.14. $C_{11}H_{21}O_2N$. Calculated %: N 7.03.

The 2,4-dinitrophenylhydrazone of this piperidone melts at 116-117° (from alcohol); the hydrochloride melts at 162-163° (from acetone).

Distillation of the neutral products gave 1.7 g of the original ketone with b.p. 95-100° at 4 mm.

Action of ammonia on 2-methoxy-5-β-ethoxyethyl-5-hexen-4-one (III, R' = C_2H_5). A mixture of 20.5 g ethoxy ketone (III, R' = C_2H_5) (b.p. 100-102° at 2 mm, n_D^{20} 1.4550 [7]), 50 g aqueous solution of ammonia, and 20 ml alcohol was saturated with gaseous ammonia at 0° (ammonia uptake 20 g), after which it was heated in a sealed ampoule at 60° for 3.5 hours. The ammonia was driven off in vacuum, at first in the cold and later with heating on a water bath at 45°. The reaction mass was acidified with 10% hydrochloric acid until weakly acidic, and the neutral products were extracted with ether. The organic bases were salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and distilled in vacuum to give 4.5 g 2-methyl-5-β-ethoxyethyl-4-piperidone (IV, R' = C_2H_5, R = H).

B.p. 103-104° at 5 mm, n_D^{20} 1.4668, d_4^{20} 0.9807, MR_D 52.39; calculated 51.44.
Found %: N 7.06, 7.35. $C_{10}H_{19}O_2N$. Calculated %: N 7.56.

The 2,4-dinitrophenylhydrazone of this piperidone melts at 165-167° (from alcohol).

From the neutral products was recovered the original ethoxy ketone with b.p. 110-113° at 6 mm, n_D^{20} 1.454.

Action of methylamine on 2-methoxy-5-β-ethoxyethyl-5-hexen-4-one (III, R' = C_2H_5). 13 g ketone (III, R' = C_2H_5) and 28 ml aqueous methylamine (25%) were dissolved in 15 ml ethyl alcohol and heated in a sealed ampoule for 3 hours on a water bath at 60°. After acidification with hydrochloric acid and removal of the neutral products, the flask containing the acidic solution of organic bases was connected to a reflux condenser and heated 4 hours on a water bath at 50°. The base was then salted out with potassium carbonate, extracted with ether, dried with sodium sulfate, and distilled in vacuum to give 8.1 g 1,2-dimethyl-5-β-ethoxyethyl-4-piperidone (IV, R' = C_2H_5, R = CH_3).

B.p. 109-110 at 4 mm, n_D^{20} 1.4689, d_4^{20} 0.9714, MR_D 57.05; calculated 56.39.
Found %: N 6.91, 7.18. $C_{11}H_{21}O_2N$. Calculated %: N 7.03.

The 2,4-dinitrophenylhydrazone of 1,2-dimethyl-5-β-ethoxyethyl-4-piperidone (IV, R' = C_2H_5, R = CH_3) melts at 188° (from alcohol); the hydrochloride melts at 169-170° (from acetone).

No neutral products were detected.

Action of ethylamine on 2-methoxy-5-β-ethoxyethyl-5-hexen-4-one (III, R' = C_2H_5). A mixture of 15 g ethoxy ketone (III, R' = C_2H_5) 11 g 50 % ethylamine and 5 ml ethyl alcohol in a sealed tube was heated 6 hours on a water bath at 68°. The mixture was worked up as before to give 6 g 2-methyl-1-ethyl-5-β-ethoxyethyl-4-piperidone (IV, R' = R = C_2H_5) in the form of a pale-yellowish, mobile liquid.

B.p. 113-115° at 5 mm, n_D^{20} 1.4688, d_4^{20} 0.9605, MR_D 61.76; calculated 61.01.
Found %: N 6.53; OC_2H_5 24.01. $C_{12}H_{23}O_2N$. Calculated %: N 6.57; OC_2H_5 21.12

The 2,4-dinitrophenylhydrazone of 2-methyl-1-ethyl-5-β-ethoxyethyl-4-piperidone melts at 195° (from alcohol); the hydrochloride melts at 156° (from acetone).

Neutral products were not obtained.

Action of ammonia on 2-β-butoxyethyl-5-methoxy-1-hexen-3-one (III, R' = C_4H_9). A mixture of 13 g butoxy ketone (III, R' = C_4H_9), (b.p. 126-129° at 4 mm, n_D^{20} 1.4576 [8]), 20 ml alcohol, and 50 ml aqueous ammonia solution was saturated with gaseous ammonia (ammonia uptake 20 g) and then heated in a sealed ampoule at 60° 10 hours.

Working up yielded 1.9 g 2-methyl-5-β-butoxyethyl-4-piperidone (IV, R' = C_4H_9, R = H).

B.p. 129-130° at 6 mm, n_D^{20} 1.4668, d_4^{20} 0.9556, MR_D 61.84; calculated 60.67.
Found %: N 6.34, 6.46. $C_{12}H_{23}O_2N$. Calculated %: N 6.57.

The 2,4-dinitrophenylhydrazone of 2-methyl-5-β-butyoxyethylpiperidone melts at 145° (from alcohol).

From the neutral products was obtained 4 g of original ketone (III, R' = C_4H_9), with b.p. 110-113° at 6 mm, n_D^{20} 1.454.

Action of methylamine on 2-β-butoxyethyl-5-methoxy-1-hexen-3-one (III, R' = C_4H_9). A mixture of 6.8 g butoxy ketone (III, R' = C_4H_9), 7 g aqueous solution of methylamine (24 %) and 10 ml ethyl alcohol was heated in a glass ampoule at 65° for 3 hours. The reaction mass was worked up in the usual manner to give 4.5 g 1,2-dimethyl-5-β-butoxyethyl-4-piperidone (IV, R' = C_4H_9, R = CH_3), admixed with some 1,2-dimethyl-5-β-butoxyethyl-4-methyliminopiperidine in the form of a transparent, mobile liquid with an unpleasant odor, turning yellow on standing; b.p. 129-130° at 5 mm, n_D^{20} 1.4645. To this product was added 40 g 10 % hydrochloric acid, and on the next day the mixture was heated 4 hours at 58-63°. The product was then neutralized with potassium carbonate, extracted with ether, dried with sodium sulfate, and vacuum-distilled to give 3.8 g pure 1,2-dimethyl-5-β-butoxyethyl-4-piperidone (IV, R' = C_4H_9, R = CH_3).

B.p. 115-116° at 2 mm, n_D^{20} 1.4658, d_4^{20} 0.9504, MR_D 66.15; calculated 65.43.
Found %: N 6.61. $C_{13}H_{25}O_2N$. Calculated %: N 6.17.

The hydrochloride of 1,2-dimethyl-5-β-butoxyethyl-4-piperidone melts at 157-158° (from acetone).

Action of ethylamine on 2-methoxy-5-β-butoxyethyl-5-hexen-4-one (III, R' = C_4H_9). A mixture of 13 g butoxy ketone (III, R' = C_4H_9), 7 g 50% ethylamine and 10 ml ethyl alcohol in a sealed ampoule was heated 5 hours on a water bath at 65-70°. After acidification with hydrochloric acid and removal of the neutral products, the flask containing a weakly acidic solution of the organic base was joined to a reflux condenser and heated for 4 hours on a water bath at 50°. The reaction mass was treated with potassium carbonate, and the base was extracted with ether, dried with sodium sulfate, and vacuum-distilled to give 6.2 g 2-methyl-1-ethyl-5-β-butoxyethyl-4-piperidone (IV, R' = C_4H_9, R = C_2H_5).

B.p. 137-138° at 5 mm, n_D^{20} 1.4688, d_4^{20} 0.9445, MR_D 71.06; calculated 70.25.
Found %: N 5.8, 5.9. $C_{14}H_{27}O_2N$. Calculated %: N 5.8.

The hydrochloride of this piperidone melts at 148-150° (from acetone).

Condensation of diisopropyl ketone with formaldehyde. 1.5 g metallic sodium was dissolved in 50 g methyl alcohol, and to this solution was added 50 g diisopropyl ketone and 20 g paraformaldehyde. The reaction mixture was boiled on a water bath for 6 hours and then left overnight. The next day the main bulk of the methanol was distilled off in vacuum on a water bath at 45°. The residue was neutralized with dilute hydrochloric acid, extracted with ether, dried with sodium sulfate, and distilled to give 26 g pure 2,4,4-trimethyl-5-hydroxypentan-3-one (V).

B.p. 85-86° at 16 mm, n_D^{20} 1.4430, d_4^{20} 0.9293, MR_D 41.08; calculated 40.81.

The 2,4-dinitrophenylhydrazone melts at 152-153°.

Found %: N 18.26. $C_{14}H_{20}O_5N$. Calculated %: N 17.50.

Methylation of 2,4,4-trimethyl-5-hydroxypentan-3-one (V). 20 g sodium hydroxide was dissolved in 90 ml water, 35 g 2,4,4-trimethyl-5-hydroxypentan-3-one (V) was added, and 40 g dimethyl sulfate was introduced. The mixture was stirred $1^1/_2$ hours and then left overnight. The following day the stirring was continued for another 3 hours at 40°, 20 g sodium hydroxide in 40 ml water was added, and the mixture heated 4 hours at 50°. The product was extracted with ether, dried with sodium sulfate, and fractionated in vacuum to give 8 g 2,4,4-trimethyl-5-methoxypentan-3-one (VI).

B.p. 90-92° at 25 mm, n_D^{18} 1.4300, MR_D 45.15; calculated 45.43.
Found % C 67.69, 68.03; H 11.62, 11.30; OCH_3 21.23, 20.22. $C_9H_{18}O_2$. Calc.: C68.34; H 11.38; OCH_3 19.58.

Action of an aqueous solution of dimethylamine on 2,4,4-trimethyl-5-methoxypentan-3-one (VI). A mixture of 10 g β-methoxy ketone (VI), 20 ml aqueous solution of dimethylamine (25%) and 2 ml dioxan was heated in a glass ampoule for 6 hours on a boiling water bath. The reaction mixture was worked up in the usual manner to give 8.8 g unreacted β-methoxy ketone (VI) with b.p. 83-85° at 15 mm, n_D^{20} 1.4330.

After drying and distillation of the ether extract, no organic bases were found.

Action of dry piperidine on 2,4,4-trimethyl-5-methoxypentan-3-one (VI). A mixture of 7 g methoxy ketone (VI) and 8 g dry piperidine was heated in a glass ampoule 5 hours on a boiling water bath. The reaction mixture was neutralized with dilute hydrochloric acid; the neutral products were thoroughly extracted with ether, dried with sodium sulfate, and distilled. 5.9 g unreacted methoxy ketone (VI) was recovered; b.p. 88-90° at 23 mm, n_D^{20} 1.4302.

As in the preceding experiment, no organic bases at all were formed.

Action of dimethylamine on 5-methyl-1,5-dimethoxyhexan-3-one (VII). a) 20 g 5-methyl-1,5-dimethoxyhexan-3-one (VII) (b.p. 105-107° at 15 mm, n_D^{20} 1.4734 [9]) and 40 g 24% aqueous dimethylamine were heated in a glass ampoule for 2 hours at 70°. The reaction mixture was worked up as previously to give 6.8 g 5-methyl-1-dimethylamino-4-hexen-3-one (VIII) with b.p. 90-93° at 11 mm, n_D^{20} 1.4596. The picrate of this amino ketone melted at 106° (from alcohol) and did not give a depression with an authentic specimen [2]. Neutral products were not found.

b) A mixture of 20 g dimethoxy ketone (VII) and 40 g 24% aqueous dimethylamine was left for 48 hours and then worked up as above to give 7.3 g 5-methyl-1-dimethylamino-4-hexen-3-one (VIII) with b.p. 85-88° at 12 mm, n_D^{20} 1.4600; picrate m.p. 106°.

SUMMARY

The reaction of ammonia and amines with various α-, β-, γ- and δ-alkoxy ketones was investigated and it was shown that the reaction of aminolysis with formation of the corresponding amino ketones proceeds only with β-alkoxy ketones containing hydrogen atoms in the α-position. Experimental data are submitted for the mechanism of this reaction which proceeds through detachment of alcohols from the β-alkoxy ketones, followed by addition of ammonia or amines. Wtih the help of the aminolysis reaction the synthesis was effected of 8 new 4-piperidones containing alkoxy groups.

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Institute of Chemistry
Academy of Sciences, Armenian SSR

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STUDY OF THE REACTION OF METHYL ORTHOSILICATE WITH ORGANOMAGNESIUM COMPOUNDS

SYNTHESIS OF ALKYLMETHOXYSILANES

M.G. Voronkov and A.Ya. Yakubovskaya

E.S. Khotinsky and V. Serezhenkov [1] showed that mixed organomagnesium compounds react with ethyl orthosilicate to form alkyltriethoxysilanes according to the equation:

$$Si(OC_2H_5)_4 + RMgBr \longrightarrow RSi\ (OC_2H_5)_3 + C_2H_5OMgBr$$

K.A. Andrianov and O.L. Gribanova [2] found that even a trace of ethyl orthosilicate catalyzes the formation of organomagnesium compounds, thus enabling the latter to be obtained in the absence of diethyl ether. These authors [3,5] also developed a method of synthesis of alkyltriethoxysilanes based either upon direct action on metallic magnesium of a mixture of alkyl halides and ethyl orthosilicate or upon reaction of the latter with organomagnesium compounds obtained in the absence of diethyl ether. Andrianov [6] pointed out that by changing the thermal conditions of the reaction and taking an excess of organomagnesium compound, it is possible to replace the alkyl radicals in ethyl orthosilicate by two, three and even four ethoxy groups. This possibility was also indicated by the results of A.V. Topchiev and N.S. Nametkin [7] who made an exhaustive study of the reaction of $Si(OC_2H_5)_4$ with phenyl magnesium bromide.

Following the work of Andrianov, the reaction of ethyl orthosilicate with organomagnesium compounds was studied by a number of other authors [8-18], and it formed the basis of the industrial process of synthesis of alkylethoxysilanes. By contrast the reaction of organomagnesium compounds with other esters of orthosilicic acid has been completely neglected. The only literature reference [19] is to the reaction of p-cresyl silicate with phenyl magnesium bromide and benzyl magnesium chloride; the product of this reaction, however, was p-cresol, since the reaction mixture was subjected to hydrolysis.

We have now made a study of the reaction of organomagnesium compounds with methyl orthosilicate $Si(OCH_3)_4$ with the objective of developing a method of synthesis of alkylmethoxysilanes. In the first place a search was made for the optimum conditions of the reaction leading to maximum yields of alkylmethoxysilanes. For this purpose a series of experiments was performed in which the influence of reaction conditions on the yields of alkylmethoxysilanes was examined with reference to the reaction of n-butyl magnesium bromide with methyl orthosilicate. The following seven procedures were studied.

A. Into activated magnesium iodide, taken in 5% excess, was run the methyl orthosilicate.* Dropwise addition was then made to the mixture, at first with gentle heating and later with cooling, of an equimolar amount of alkyl halide.

B. Dropwise addition was slowly made to activated magnesium iodide of a mixture of methyl orthosilicate and alkyl halide. In this case the reaction was more vigorous and much heat was released. The reaction was performed with periodic cooling.

C. To an equimolar mixture of methyl orthosilicate and alkyl halide was added pulverized magnesium in small portions.

D. Methyl orthosilicate was added dropwise with cooling to the organomagnesium compound prepared in a medium of anhydrous diethyl ether.

E. 1 ml methyl orthosilicate was added as a catalyst to activated magnesium iodide; dropwise addition was then made of half of the required amount of alkyl halide. The second half was added in the form of a 15% solution in benzene. The methyl orthosilicate was added dropwise with cooling to the so-prepared organomagnesium compound.

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* We found that methyl orthosilicate catalyzes the reaction of primary alkyl bromides and benzyl chloride with magnesium.

F. To a mixture of equal volumes of methyl orthosilicate and anhydrous diethyl ether was added a previously prepared ether solution of the organomagnesium compound.

G. In experiments with molar rations of $Si(OCH_3)_4 : C_4H_9MgBr$, of 1:2, 1:3, 1:4 and 1:5, the syntheses were effected by method B, but with addition to the reaction mixture of an inert solvent (benzene or dearoamtized kerosenewith b.p. above 220°). The remaining experimental conditions were identical for all the methods.

Experiments carried out by these methods at molar ratios of $Si(OCH_3)_4 : C_4H_9MgBr$ 1:1 showed that the above-mentioned changes of conditions of synthesis have no substantial influence upon the yields of final reaction products which are butyltrimethoxysilane and dibutyldimethoxysilane. Their maximum yields are respectively 20 and 31% of the theoretical. It follows from this that the reaction of organomagnesium compounds with an equimolar amount of methyl orthosilicate leads very much more readily to the formation of dialkyl-substituted derivatives $R_2Si(OCH_3)_2$, in consequence of which a considerable proportion of the ester (up to 34%) does not enter into reaction. This indicates that alkyltrimethoxysilanes react with alkyl magnesium halides with very much greater facility than tetramethoxysilane itself, i.e. that the reactivity of a molecule in presence of RMgX is determined not by the number of reactive CH_3O groups but by the structure of the molecule as a whole.

In the later course of the work we mainly utilized methods B and G, which are most convenient and simple in execution.

On increasing the molar ratio of $Si(OCH_3)_4 : C_4H_9MgBr$ to 2 in synthesis by method G, the yield of butyltrimethoxysilane could not be raised beyond 16-20%. The yields of butyltrimethoxysilane at the same time remained smaller than the yields of dibutyldimethoxysilane.

With a ratio of $Si(OCH_3)_4 : C_4H_9MgBr$ of 1:3, it was possible to raise the maximum yield of dibutyldimethoxysilane to 38%, while at a 1:5 ratio the yield of tributylmethoxysilane was 12%.

Formation of tetrabutysilane was never observed in any of the reactions of butyl magnesium bromide with methyl orthosilicate. We likewise failed to obtain tetrabutylsilane in the reaction of butyl magnesium bormide with ethyl orthosilicate, contrary to the claim of Post and Hofrichter[10], who obtained tetrabutysilane in 56% yield by the latter route. These data are extremely dubious, since the authors did not carry out analyses of the prepared tetrabutylsilane, and its constants have nothing in common with the constants of pure tetrabutylsilane [20] but approximate to the constants of the tributylethoxysilane previously described by us [20].

In a study of the influence of the nature of the halogen in the starting alkyl halides upon the couse of their reaction with magnesium and methyl orthosilicate it was found that none of the alkyl chlorides (except benzyl chloride) reacts with magnesium in presence of methyl orthosilicate as catalyst under the conditions of procedures A, B, C, E, and G. Consequently alkylmethoxysilanes can be synthesized from alkyl chlorides only by procedures D and F, i.e., under conditions of their preliminary transformation into organomagnesium compounds in a medium of anhydrous ether.

With the objective of establishing the optimum conditions for preparation of alkylmethoxysilanes from alkyl chlorides by procedure F, we studied the relation between yields of methylmethoxysilanes, in the reaction between methyl orthosilicate and methyl magnesium chloride, and the molecular ratio of the two components. Here also the yields of dialkyldimethoxysilanes were higher in all cases than the yields of monoalkyl derivatives; the yields of dimethyldimethoxysilane and of trimethylmethoxysilane were quite high, up to 44% [with $Si(OCH_3)_4 : CH_3MgCl = 2$] and 53% [with $Si(OCH_3)_4 : CH_3MgCl = 3.5$]. In syntheses of alkylmethoxysilanes from alkyl iodides, the latter react extremely vigorously with magnesium in a medium of methyl orthosilicate. In this case, however, the reaction leads mainly to formation of solid products which did not distil in vacuum and were not further examined.

We also studied the influence of the structure of the alkyl radical in the magnesium alkyl halides upon their reaction with methyl orthosilicate (mainly using procedure D); it was found that alkyl magnesium halides containing a tertiary alkyl radical (tert-C_3H_9MgCl) do not react with methyl orthosilicate (or with ethyl orthosilicate). In the case of secondary alkyl (sec-C_4H_9Br) and of aryl (C_6H_5MgBr) radicals the reaction proceeds sluggishly by all procedures and the yields of substituted derivates are low. Alkyl magnesium halides containing primary radicals with normal structure, CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, also $CH_2{=}CHCH_2-$ and $C_6H_5-CH_2-$, react smoothly with methyl orthosilicate, the reaction being most vigorous in the cases of benzyl magnesium chloride and allyl magnesium chloride. In the reaction of methyl orthosilicate with isoamyl magnesium bromide the formation of isoamylmethoxysilane was not observed (only diisoamyl was isolated). In the table are set forth the physical constants, analytical data and yields of the alkylmethoxysilanes, 8 of which were previously unknown.

Physical properties, analyses and yields of alkylmethoxysilanes

Formula	Boiling point (at 760 mm)	d_4^{20}	n_D^{20}	$(n_F^{20} - n_C^{20}) \cdot 10^4$	γ^{20}	Si content (in %)		Molecular weight		Yield (in %)	Procedure	Molar ratio of RMgX : $Si(OCH_3)_4$
						Calculated	Found	Calculated	Found			
$CH_3Si(OCH_3)_3$	103.5°	0.9489	1.3696	-	-	20.62	20.55, 20.50	136.22	-	13	F	1
$n\text{-}C_4H_9Si(OCH_3)_3$ *	164.8	0.9312	1.3979	68	23.72	15.75	15.71, 15.42	178.30	175.0, 175.1	18-20	B, C, F	1
$n\text{-}C_8H_{17}Si(OCH_3)_3$ *	181.9	0.9199	1.4030	72	23.85	14.60	14.47, 14.28	192.33	194.4, 190.7	26	B	1
$C_6H_5Si(OCH_3)_3$	102 (20 mm)	1.064	1.4734	-	-	14.17	13.90, 13.85	198.29	-	5	E	3
$C_6H_5CH_2Si(OCH_3)_3$ *	227.7	1.064	1.4590	114	29.92	13.23	13.01, 13.00	212.32	208.2, 207.7	10	B	1
$(CH_3)_2Si(OCH_3)_2$	82.0	0.8535	1.3679	-	-	23.36	23.40, 23.47	120.22	-	44	F	2
$(n\text{-}C_3H_7)_2Si(OCH_3)_2$ *	169.3	0.8764	1.4088	76	23.68	15.93	15.79, 15.72	176.32	175.4, 173.2	36	E	1
$(n\text{-}C_4H_9)_2Si(OCH_3)_2$ *	205.4	0.8731	1.4188	76	24.74	13.74	13.70, 13.63	204.38	207.6, 209.3	38	G	3
$(n\text{-}C_8H_{17})_2Si(OCH_3)_2$ *	236.9	0.870	1.4235	75	25.10	12.08	11.96, 11.59	232.43	229.0, 225.9	35	B	1
$(CH_3)_3SiOCH_3$	57.2	0.7560	1.3678	-	-	26.95	-	104.22	-	53	F	3, 5
$(n\text{-}C_4H_9)_3SiOCH_3$ *	239.0	0.8316	1.4329	84	-	12.19	12.03, 11.60	230.46	234.7, 228.1	12	G	5
$(CH_2{=}CHCH_2)_3SiOCH_3$ *	191.2	-	1.4480	111	24.95	15.40	15.68, 15.37	182.33	180.3, 185.4	11	B	3

* New compound.

EXPERIMENTAL

(with participation of N.A. Dmitrieva)

Starting components. Methyl orthosilicate was prepared by the literature method [21] and purified by distillation through a column over sodium; it then had b.p. 121.5° (764 mm), d_4^{20} 1.034, n_D^{20} 1.3689. Metallic magnesium was first dried over phosphorus pentoxide. Methyl chloride was taken from a cylinder and before reaction it was passed through a concentrated sulfuric acid washbottle. The remaining alkyl halides were the same preparations as those described in one of our papers [20]. Diethyl ether and benzene (thiophene-free) were purified and dehydrated by the usual method. Dearomatized kerosene was obtained by prolonged shaking with concentrated sulfuric acid of a petroleum fraction with b.p. 220-270°, followed (after washing and drying) by distillation over metallic sodium in vacuum.

Method of investigation. All the syntheses were carried out in parallel in two apparatuses, consisting of a round-bottomed flask fitted with mechanical stirer with mercury seal, dropping funnel and reflux condenser joined to a clacium chloride tube. In all the experiments 38.1 g (0.25 mole) methyl orthosilicate was introduced into reaction, while the magnesium was taken in 5% excess. The reaction was completed by 5-hours' heating of the reaction mixture on a water bath. The reaction products were distilled off from the same flask, preferably in vacuum. The distilled mixture of volatile reaction products was fractionated in an analytical column with an efficiency of 12 theoretical plates. The separated substances were redistilled through the same column over metallic sodium. The heart portions of constant-boiling fractions were taken for determination of physical constants. *

SUMMARY

The reaction of methyl orthosilicate with organomagnesium compounds was studied. It was shown that methyl orthosilicate, like ethyl orthosilicate, is a catalyst for the formation of organomagnesium compounds from magnesium and primary alkyl bromides as well as benzyl chloride. In this case the synthesis of alkylmethoxysilanes is effected by direct reaction of magnesium sium with alkyl bromide and methyl orthosilicate in the absence of diethyl ether, avoiding the stage of preparation of organomagnesium compound. Alkyl chlorides are unsuitable for such syntheses and must previously be converted into the alkyl magnesium halides. It was shown that in the reaction of organomagnesium compounds with methyl orthosilicate, dialkyldimethoxysilanes are formed with very much greater facility than alkyltrimethoxysilanes . 12 alkylmethoxysilanes were synthesized, 8 of which were formerly unknown.

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* The procedure for determination of physical constants and molecular weight has been described before [20]. Silicon was determined by mineralization with a mixture of oleum and fuming nitric acid followed by calcination of the SiO_2 at 1000°.

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THE BEHAVIOR OF THE SILICON – CARBON BOND IN α-ALKYNYL – AND β-ALKENYISILANES TOWARD CHEMICAL REAGENTS

A.D. Petrov and L.L. Shchukovskaya

In the case of aryl- and alkylsilanes synthesized some considerable time ago, as well as of their derivatives containing halogens or other functional groups, we have much data characterizing the stability of the Si–C bond. This stability varies widely both with the nature of the reagent and with changes in the structure of silanes, as well as with the reaction conditions.

In an investigation of the behavior toward HCl of a large number of aryl-silanes it was shown [1] that the silicon–carbon bond is less stable here than in alkylsilanes, and that the stability of the Si–C bond toward acid increases in the following order: p-tolyl < phenyl < p-chlorophenyl < benzyl. It was also shown that concentrated sulfuric acid is capable [2] of splitting off one CH_3 group from compounds containing the $(CH_3)_3Si$ grouping and a functional group at the carbon in the beta-position to the silicon in the fourth radical, for example:

$$2(CH_3)_3Si-CH_2-CH_2-COOH \xrightarrow[H_2O]{H_2SO_4} [HOOC-CH_2-CH_2-Si(CH_3)_2]O + 2CH_4.$$

A.D. Petrov and V.F. Mironov [3] investigated the decomposition of β-halosilanes $R_3Si-C-C-X$ under the action of R_1MgX and showed that the course of the reaction according to schemes (1) and (2)

$$R_3Si-C-C-X + R_1MgX \rightarrow R_3Si-R_1 + C=C \quad (1)$$

$$R_3Si-C-C-X + R_1MgX \rightarrow R_3Si-C-C-R_1 \quad (2)$$

is governed to a greater or lesser extent both by the nature of R, X and R_1, and by the thermal conditions of these reactions, etc.

The behavior toward chemical reagents of the Si–C bond in the case of alkynyl- and alkenylsilanes has been very little studied because it is only recently that these compounds have been synthesized. Even the very possibility of obtaining compounds containing the SiC≡C grouping had been questioned until quite recently. These doubts were resolved, however, when we [4], and, simultaneously and independently, Frisch and Young [5], succeeded in demonstrating the possibility of formation of diverse compounds of the types of $R_3SiC{\equiv}CSiR_3$ and $R_3SiC{\equiv}C-R'$.

In the present investigation we set out to synthesize the higher homologs of the $R_3SiC{\equiv}CSiR$ series, in particular with utilization of R_3SiF in place of R_3SiCl; we also wished to study the possibility of hydrating the triple bond in the alpha-position to the silicon, to examine the addition of bromine at the triple bond in the alpha-position and at the double bond in the beta-position to the silicon, and also to test the possibility of interaction of $SiCl_4$ with XMgC≡CR.

The relatively low yield of $(C_4H_9)_3SiC{\equiv}CSi(C_4H_9)_3$ when using $(C_4H_9)_3SiCl$ in the synthesis, and the contamination with $(C_4H_9)_3SiOSi(C_4H_9)_3$, which could be formed from unreacted $(C_4H_9)_3SiCl$ during hydrolysis of the reaction products, prompted us to turn to the fluorosilanes in the case of condensation of the Iotsich complex with high-molecular trialkylhalosilanes. Fluorosilanes have been successfully applied in the synthesis of tetraalkyl- and tetraarylsilanes whose preparation necessitates the overcoming of the steric hindrance [5] (tetraisopropylsilane, tetra-α-naphthylsilane, etc.). Substitution of chlorine by fluorine in R_3SiX permitted the preparation in good yields of $(C_4H_9)_3SiC{\equiv}CSi(C_4H_9)_3$ and $(C_6H_{13})_3SiC{\equiv}CSi(C_6H_{13})_3$ and the realization of the synthesis of the aromatic disilane $(C_6H_5)_3SiC{\equiv}CSi(C_6H_5)_3$. Furthermore the stability to hydrolysis of the R_3SiF that we used and their inability to give silanol and disiloxane on saponification permitted us to throw more light on the mechanism of their condensation with Iotsich's reagent. This reagent, like all Grignard reagents, is a complex of an alkyl magnesium halide with an ether. Also in this case – in condensation carried out at elevated temperatures – the reaction was found to proceed according to the over-all equation (which does not indicate the mechanism):

$$6R_3SiX + (C_2H_5)_2O \cdot XMgC{\equiv}CMgX \cdot O(C_2H_5)_2 \xrightarrow{(C_2H_5)_2O}$$

$$\longrightarrow 2R_3SiOC_2H_5 + R_3SiC{\equiv}CSiR_3 + R_3SiOSiR_3 + 2C_2H_5X + 2MgX_2.$$

i.e., with formation not only of di-trialkylsilyl-acetylene but also of trialkylethoxysilane and of hexaalkyldisiloxane. We observed formation of the latter only when R = C_4H_9 and C_6H_{13}. Evidently with increasing size of R, steric difficulties are introduced and the anomalous condensation of R_3SiX with diethyl ether, caused by the tendency of silicon to form the Si–O bond, proceeds with greater facility.

The ability of chlorosilanes to react with diethyl ether (which leads to contamination of the products of synthesis) was already noted by Kipping [7] and his co-workers who suggested that this reaction proceeds according to the equation: $SiCl_4 + (C_2H_5)_2O \rightarrow Cl_3SiOC_2H_5 + C_2H_5Cl$. Our experiments confirmed this hypothesis. Only an increase of the excess of Iotsich's reagent by 10-12 times leads to formation of high-molecular acetylenic disilanes. Evidently in such condensations we have a number of competing equilibrium reactions, and with increasing excess of Iotsich complex the formation of disiloxane is suppressed in favor of the formation of the disilane (di-trialkyl-silyl-acetylene).

If the diethyl ether is replaced by ligroin (34-50°) after formation of the Iotsich complex, then as previously the formation of $R_3SiOC_2H_5$ is observed at the expense of the combined ether in the acetylene dimagnesium dibromide, but its yield is slightly reduced. This indicates that the diethyl ether used as a solvent also participates in the formation of $R_3SiOC_2H_5$.

Unlike the liquid aliphatic R_3SiX, crystalline triphenylfluorosilane does not condense with diethyl ether under similar conditions and does not fully enter into reaction, $(C_6H_5)_3SiF$ being recovered unchanged.

In order to obtain evidence of the participation of diethyl ether in the formation of $R_3SiOC_2H_5$, we decided to effect the condensation of R_3SiX with Iotsich's complex, first obtained in absence of diethyl ether, in benzene. Under the conditions employed, the reaction proceeds with formation of 15-18% yield of the corresponding acetylenic disilane even with a $2\frac{1}{2}$-fold excess of acetylene dimagnesium dibromide. Partly unreacted R_3SiX, as in the case of $(C_6H_5)_3SiF$, is recovered unchanged.

All attempts to effect the hydration of acetylenic disilanes and monosilanes proved in vain. The disilanes evidently either undergo breakdown at the silicon–carbon bond with formation of intermediate complexes with mercury salts which subsequently hydrolyze

$$R_3SiC{\equiv}CSiR_3 \xrightarrow[HgSO_4]{2HOH} 2R_3SiOH + HC{\equiv}CH \rightarrow R_3SiOSiR_3$$

or formation takes place of ketones with a carbonyl in the β-position, and these break down according to the equation:

$$R_3Si{-}C{\equiv}C{-}SiR_3 + H_2O \longrightarrow R_3Si\overset{OH}{\overset{|}{-}}\overset{H}{\overset{|}{C}}H_2CO\overset{H}{\overset{|}{-}}\overset{OH}{\overset{|}{C}}SiR_3 \longrightarrow 2R_3SiOH + CH_3C\begin{matrix}{\diagup\!\!\!\diagup}O\\ \diagdown H\end{matrix}$$

This mechanism was confirmed in the case of hydrolysis of $R_3Si{-}C{\equiv}C{-}C_6H_5$, which gave acetophenone. Bromination of $(CH_3)_3Si{-}C{\equiv}C{-}Si(CH_3)_3$ gave only the dibromide $(CH_3)_3Si{-}CBr{=}CBr{-}Si(CH_3)_3$ [5], while bromination of $(C_2H_5)_3Si{-}C{\equiv}C{-}CH_3$ likewise gave a tribromide in accordance with the equation:

$$(C_2H_5)_3Si{-}CBr_2CBr_2{-}CH_3 \longrightarrow HBr + (C_2H_5)_3Si{-}CBr_2{-}CBr{=}CH_2.$$

Consequently the triple bond in the alpha-position (in complete analogy with the double bond in the same position) proved extremely stable toward bromine, and the Si–C bond was not broken under the action of bromine. Moreover, the presence of the triple bond in the alpha-position (fully analogous to the double bond in vinylsilanes) raised the resistance of the Si–C bond toward bromine.* At the same time the shift of the double bond to the beta-position (in a series of allylsilanes) was found to considerably lower the stability of the silicon–carbon bond, as was established by titration with bromine of diverse allylsilanes in the conditions of the Kaufmann reaction (see table).

It is not difficult to see that, as a rule, the bromine consumption is $1\frac{1}{2}$-2 times higher than would have been the case if bromine had only added on at the double bond. The partial rupture of the Si–C bonds can be represented by the equation:

$$(CH_2{=}CH{-}CH_2)_4Si + 6Br_2 \longrightarrow 2BrCH_2{-}CHBr{-}CH_2Br + (BrCH_2{-}CHBr{-}CH_2)_2SiBr_2,$$

$$\text{or } (BrCH_2{-}CHBr{-}CH_2)_2Si(OCH_3)_2 + 2HBr.$$

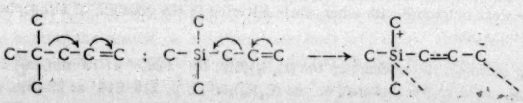
This type of beta-breakdown of allysilanes had already been observed by A.D. Petrov and V.F. Mironov [8] in the case of triethylallylsilane. The ease of breakdown of alkenylsilanes with a double bond in the beta-position to the silicon

* Compare for instance the behavior of a solution of bromine in CCl_4 toward $(CH_3)_3Si{-}C_6H_5$ [11].

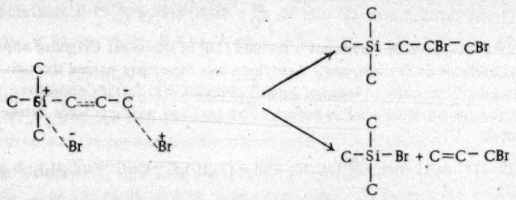
Bromine numbers in Kaufmann's reaction

Compound	Bromine numbers		
	Calculated without decomposition	Found	Calculated according to the equation
α-$C_{10}H_7-Si(CH_2CH=CH_2)_3$	172.6	287.54	287.70
n-$C_4H_9-Si(CH_2CH=CH_2)_3$	230.7	395.0	384.6
$C_6H_{11}-Si(CH_2CH=CH_2)_3$	205.0	278.0	273.5
$(n\text{-}C_4H_9)_3Si-CH_2CH=CH_2$	66.6	131.31	133.32
$(CH_2=CH-CH_2)_4Si$	333.3	496	500.0
$(C_6H_5)_3Si-CH_2CH=CH_2$	53.3	95.6	106.6

under the action of bromide is undoubtedly associated with the ease of addition of acids and thiocyanogen at this bond. The velocity of addition of thiocyanogen to monoalkenylsilanes with a primary-secondary double bond in the alpha-, beta-, gamma- and delta-positions has been studied by A.A. Bugorkova and co-workers [9]. It was found that the addition of thiocyanogen at double bonds in the alpha-, gamma- and delta-positions takes place more slowly than in the case of addition to olefins, about 24 hours being required for completion of the process. On the other hand, the addition of thiocyanogen at the beta-bond, which proceeds without rupture of the Si−C bond, is completed in several minutes. We can therefore state that the replacement, for example, in trialkylallylmethanes of the fourth carbon by silicon sharply accelerates thiocyanation. We suggest that this is due to polarization of the silicon−carbon bond (which thus becomes, as it were, intermediate between a single and a double bond), the system of allyl and silicon in allylsilanes thus being similar to a conjugaged system: Si−C−C=C. Furthermore, whereas in a hydrocarbon the electrons are shifted to the double-bonded carbon at the end of the chain



in the silicohydrocarbon of analogous structure, on the other hand, they are shifted to the silicon. This electron shift is possibly also accompanied by valence isomerism (as this phenomenon was named by Wheland), i.e. partial shift of the double bond in the direction of the polar element. A system is consequently formed in which the addition of bromine in the 1,4-position is facilitated, i.e. addition to Si and to the end carbon, in full analogy to what happens in butadiene.



These facts may also provide an explanation of the greater facility of addition of thiocyanogen to allylsilanes, as well as of the breakdown of the latter during Kaufmann bromination.

The double bond in the beta-position also differs markedly from the double bond in the alpha-position in respect of its behavor toward aryllithiums. Whereas C_6H_5Li adds on to $(C_6H_5)_3Si-CH=CH_2$ according to the scheme:

$$(C_6H_5)_3Si-CH=CH_2 + LiC_6H_5 \longrightarrow (C_6H_5)_3Si-\underset{Li}{CH}-CH_2-C_6H_5 \xrightarrow{H_2O} (C_6H_5)_3Si-CH_2-CH_2-C_6H_5,$$

phenyllithium does not add on at the double bond of the triphenylallylsilane (synthesized for the first time) but apparently forms a complex. Decomposition of the complex with water results first in decomposition of LiC_6H_5 with formation of LiOH, and subsequently in decomposition of the original allylsilane with formation of $(C_6H_5)_3SiOH$.

EXPERIMENTAL

Syntheses of $(C_4H_9)_3Si-C\equiv C-Si(C_4H_9)_3$. 1. In the usual apparatus for Grignard sysnthesis was prepared acetylene dimagnesium dibromide from 20.0 g magnesium, 94.0 g ethyl bromide and acetylene (passed through for 25 hours) in anhydrous diethyl ether. To the reaction flask was then added 48.0 g $(n\text{-}C_4H_9)_3SiCl$, and the contents of the flask were boiled for 6 hours; the ether was driven off and the residue heated on an oil bath (140-160°) for 26 hours. After cooling, the contents of the flask were decomposed with water, and the ethereal layer was separated and dried; the residue was fractionated to give two fractions. In physical properties and analytical data the 1st fraction corresponded to $(C_4H_9)_3SiOC_2H_5$, yield 32% reckoned on the $(n\text{-}C_4H_9)_3SiCl$.

B.p. 126-128° at 13 mm, n_D^{20} 1.4368, d_4^{20} 0.8217.
Found %: C 69.18, 69.32; H 13.16, 13.17; Si 10.57, 10.87. $C_{14}H_{32}OSi$. Calculated %: C 68.85; H 13.11; Si 11.47.

Treatment with conc. H_2SO_4 and water transforms the butylethoxysilane into hexabutyldisiloxane.

The 2nd fraction corresponded in physical properties and analytical data to $(C_4H_9)_3Si-O-Si(C_4H_9)_3$, yield 52% reckoned on the $(n-C_4H_9)_3SiCl$; b.p. 184-186°, n_D^{20} 1.4479, d_4^{20} 0.8362.

2. Experiment using the same method. Reactants were 60.0 g magnesium, 281.0 g ethyl bromide, acetylene (passed through for 20 hours) and 670 g tributylchlorosilane in diethyl ether. Appropriate treatment gave two fractions.

The first fraction corresponded to $(C_4H_9)_3SiOC_2H_5$, yield 43% reckoned on the $(C_4H_9)_3SiCl$; b.p. 132-134° at 27 mm (241-242° at 757 mm), n_D^{20} 1.4350, d_4^{20} 0.8229; the second fraction corresponded to $(C_4H_9)_3Si-C\equiv C-Si(C_4H_9)_3$, yield 13% reckoned on the $(C_4H_9)_3SiCl$.

B.p. 215-218° at 22 mm, n_D^{20} 1.4568, d_4^{20} 0.8339, MR_D 138.03; calculated 140.16.
Found %: C 72.88, 72.85; H 13.01, 13.24; Si 12.05. $C_{26}H_{54}Si_2$. Calculated %: C 73.9; H 13.1; Si 13.3.

3. Acetylene dimagnesium dibromide was prepared from 50.0 g magnesium, 234.0 g ethyl bromide and acetylene (passed through for 20 hours) in anhydrous diethyl ether. Addition was then made of 44.0 g $(C_4H_9)_3SiF$ and 2 g cuprous chloride. The contents of the flask were boiled, the ether distilled off and the residue heated 8½ hours at 165-170°. After cooling, the reaction products were extracted with ether while filtering in the absence of atmospheric moisture. Two fractions were isolated by fractionation.

1st fraction – $(C_4H_9)_3SiOC_2H_5$, yield 48.7% reckoned on the $(C_4H_9)_3SiF$; b.p. 128.5° at 13 mm, n_D^{20} 1.4350; 2nd fraction – $(C_4H_9)_3Si-C\equiv C-Si(C_4H_9)_3$, yield 22.3% reckoned on the $(C_4H_9)_3SiF$; b.p. 216-218° at 22 mm, n_D^{20} 1.4597.

4. After acetylene dimagnesium dibromide had been prepared under the same conditions and with the same amounts of components, the ether was removed from the flask by decantation and replaced by dry ligroin. The remaining conditions and the method of working up were the same as in the preceding experiment. Two fractions were isolated:

1st – $(C_4H_9)_3SiOC_2H_5$, yield 40.6%; b.p. 141° at 29 mm, n_D^{20} 1.4346, d_4^{20} 0.8193; 2nd – $(C_4H_9)_3Si-C\equiv C-Si(C_4H_9)_3$, yield 33%; b.p. 217-219° at 12.5 mm, d_4^{20} 0.8276, n_D^{20} 1.4595, MR_D 139.79; Calculated: 140.15.

5. Ethyl magnesium bromide was prepared by Andrianov's method [10] in the usual Grignard apparatus from 15.0 g magnesium and 100.0 g ethyl bromide in dry benzene. Acetylene was thereupon passed through the reaction flask for 12 hours. The resultant viscous, lilac-colored layer of Iotsich complex was further condensed with 39.0 g $(n-C_4H_9)_3SiF$. The remaining conditions of synthesis were as before. The reaction products were extracted with dry ligroin. Two fractions were separated:

1st – $(C_4H_9)_3SiOC_2H_5$; b.p. 112-115° at 11 mm, n_D^{20} 1.4270; 2nd – $(C_4H_9)_3Si-C\equiv C-Si(C_4H_9)_3$; b.p. 210-212° at 11 mm, n_D^{20} 1.4600.

An intermediate fraction (5 g) was also isolated with b.p. 123-125° at 11 mm, n_D^{20} 1.4370, consisting of tributylethoxysilane which was formed at the expense of the ethoxy groups of the $Si(OC_2H_5)_4$ used as a catalyst in the synthesis of ethyl magnesium bromide.

Syntheses of $(C_6H_{13})_3Si-C\equiv C-Si(C_6H_{13})_3$. 1. Reactants were 22.5 g magnesium, 100.0 g ethyl bromide, acetylene (passed through for 18 hours), 2.0 g cuprous chloride and 40.0 g trihexylchlorosilane. The conditions of synthesis were as usual. At the close of the reaction the flask contents were decomposed with water and worked up in the usual way to give two fractions:

1st – $(C_6H_{13})_3SiOC_2H_5$, yield 51% reckoned on the $(C_6H_{13})_3SiCl$; b.p. 191-192° at 12 mm, n_D^{20} 1.4442, d_4^{20} 0.8272; 2nd – $(C_6H_{13})_3Si-O-Si(C_6H_{13})_3$, yield 25%; b.p. 277-279° at 8.5 mm, n_D^{20} 1.4574, d_4^{20} 0.8385.

2. Reaction was effected under similar conditions of acetylene dimagnesium dibromide (prepared from 7.5 g magnesium, 370 g ethyl bromide and acetylene (passed through for 11 hours) in diethyl ether with 30.5 g trihexylfluorosilane. After decomposition of the residue with water and the usual treatment, two fractions were obtained.

1st – $(C_6H_{13})_3SiOC_2H_5$, yield 33%, reckoned on the $(C_6H_{13})_3SiF$; b.p. 198-202° at 19 mm, n_D^{20} 1.4447; 2nd – $(C_6H_{13})_3Si-O-Si(C_6H_{13})_3$, yield 46%; b.p. 246-247° at 3 mm, n_D^{20} 1.4554, d_4^{20} 0.8391, MR_D 188.3; calculated 187.8.
Found %: C 75.93, 75.71; H 13.42, 13.44; Si 9.76, 10.04. $C_{36}H_{78}OSi_2$. Calculated %: C 75.72; H 13.63; Si 9.79.

3. Acetylene dimagnesium dibromide was prepared from 30.0 g magnesium, 140.0 g ethyl bromide and acetylene (passed through for 18 hours) in diethyl ether. The ether was then removed by decantation and to the flask were added 300 ml dry ligroin (30-70°), 2 g cuprous chloride and 31.5 g $(C_6H_{13})_3SiF$. After the usual working up the reaction products were extracted with dry ligroin and fractionated into two fractions:

1st – $(C_6H_{13})_3SiOC_2H_5$, yield 35% reckoned on the $(C_6H_{13})_3SiF$; b.p. 197.5-199° at 17 mm, n_D^{20} 1.4440, d_4^{20} 0.8273, MR_D 105.51; calculated 105.12.

2nd – $(C_6H_{13})_3Si-C\equiv C-Si(C_6H_{13})_3$, yield 30.7%; b.p. 303-305° at 30 mm, n_D^{20} 1.4602, d_4^{20} 0.8354, MR_D 193.87; calculated 195.70.

Synthesis of $(C_6H_5)_3Si-C\equiv C-Si(C_6H_5)_3$. Condensation was effected in the usual manner of acetylene dimagnesium dibromide (prepared from 11.0 g magnesium, 52.0 g ethyl bromide and acetylene (passed through for 15 hours) in diethyl ether with 40.0 g $(C_6H_5)_3SiF$. After the ether had been distilled off, the residue was heated on a boiling water bath for 9 hours; after cooling it was decomposed with water. After the usual treatment, fractionation gave a fraction with b.p. 206° at 11.5 mm, m.p. 63° (recrystallized from ether). A mixed test with $(C_6H_5)_3SiF$ did not give a depression. The flask residue was recrystallized twice from benzene and once from ligroin (70-90°) to give crystals with m.p. 155°. Yield 13% on the $(C_6H_5)_3SiF$.

Found %: C 84.83, 84.77; H 5.78, 5.63; Si 9.87, 9.78, $C_{38}H_{30}Si_2$. Calculated %: C 84.13; H 5.5; Si 10.3.

Synthesis of $(C_6H_5)_3Si-CH_2-CH=CH_2$. Triphenylallylsilane was prepared by Yavorsky's method from 12.0 g magnesium, 61.0 g allyl bromide, and 350 g $(C_6H_5)_3SiF$ in ether. The reaction was completed by distilling off the ether from the flask and heating the residue on a boiling water bath for 9 hours. Decomposition of the residue followed by the usual treatment gave 28.0 g crystals which after recrystallization from ethanol had m.p. 91-92°. Yield 74% reckoned on the $(C_6H_5)_3SiF$.

Found %: C 83.60, 83.65; H 6.83, 6.75; Si 9.31, 8.72. $C_{21}H_{20}Si$. Calculated %: C 84.0; H 6.66; Si 9.33.

Addition of phenyllithium to $(C_6H_5)_3Si-CH_2-CH=CH_2$. To the phenyllithium prepared from 0.5 g lithium and 5.0 g bromobenzene was added 4.6 g triphenylallylsilane. The mixture was stirred at room temperature for 23 hours and was heated for 4 hours on a water bath; after that it was hydrolyzed with acidified water. The ether layer was collected and dried with Na_2SO_4; after removal of the ether the solid residue was thrice recrystallized from ligroin (60-90°) to give crystals with m.p. 149-150°.

Found %: C 80.08, 78.77; H 6.26, 6.49; Si 9.81, 9.00. $C_{18}H_{16}SiO$. Calculated %: C 78.3; H 5.8; Si 10.1.

Bromination of $(C_2H_5)_3Si-C\equiv C-C-CH_3$. Into a flask fitted with a mechanical stirrer was introduced 17.95 g $(C_2H_5)_3Si-C\equiv C-CH_3$, dissolved in 50 ml CCl_4; with energetic stirring dropwise addition was then made of bromine. After 4 hours 21.0 g bromine had combined. The last portion did not decolorize after overnight standing. The solvent was removed and the residue fractionated to give 12.0 g dibromide.

B.p. 146.5-148.5° at 23.5 mm, n_D^{20} 1.5258, d_4^{20} 1.4176, MR_D 67.97; calculated 68.12.
Found %: C 34.12, 33.96; H 5.72, 5.56. $C_9H_{16}SiBr_2$. Calculated %: C 34.50; H 5.70.

The 12.0 g of high-boiling fraction was further brominated with heating to 40-50°. In all, a further 10.5 g bromine was added. Fractionation gave 15.0 g tribromide.

B.p. 164-165° at 9 mm, n_D^{20} 1.5595, d_4^{20} 1.6766, MR_D 75.74; Calculated 76.00.
Found %: C 27.19, 17.12; H 4.26, 4.35. $C_9H_{17}SiBr_3$. Calculated %: C 27.40; H 4.40.

Hydration of $(CH_3)_3Si-C\equiv C-C_6H_5$. a) In a flask, fitted with stirrer and reflux condenser, was placed a mixture of 1.0 g $HgSO_4$, 60 ml 80% methanol and 2 drops conc. H_2SO_4. At 60° addition was made of 10.4 g $(CH_3)_3Si-C\equiv C-C_6H_5$. The mixture was heated $4\frac{1}{2}$ hours at 60°. The precipitate of catalyst was filtered off, the methanol was taken off from the filtrate in vacuum, and the residue was diluted with ether and neutralized with sodium carbonate solution. The ethereal layer was collected and dried with Na_2SO_4; the ether was removed and the residue distilled to give 5.5 g acetophenone, b.p. 103° at 33 mm, n_D^{20} 1.5313, d_4^{20} 1.0287. On standing, the product crystallized. M.p. 20°. No depression in mixed test with acetophenone.

b) A similar procedure was applied for the hydration of 7.5 g $(C_2H_5)_3Si-C\equiv C-C_6H_5$, which was introduced dropwise into a heated mixture (60°) of 1.0 g $HgSO_4$ and 50 ml 90% methanol. 4.0 g acetophenone was separated.

Synthesis of $(C_6H_5)_3Si-C\equiv C-CH_3$. Methylethynyl magnesium bromide, prepared from 5.0 g magnesium, 22.0 g ethyl bromide and 7.0 l propyne in anhydrous diethyl ether, was condensed with 28.0 g $(C_6H_5)_3SiF$ by the usual procedure with heating on a boiling water bath followed by hydrolysis. 16.5 g crystals (after recrystallization from alcohol) were collected with m.p. 113-114°. Yield 55% on the $(C_6H_5)_3SiF$.

Found %: C 84.09, 84.04; H 5.89, 6.08; Si 8.83, 8.32. $C_{21}H_{18}Si$. Calculated %: C 84.56; H 6.04; Si 9.39.

Synthesis of $Cl_3Si-C\equiv C-C_6H_5$. An Iotsich complex was prepared in the usual way from 5.0 g magnesium, 30.0 g ethyl bromide and 22.4 g phenylacetylene in anhydrous diethyl ether. After $2\frac{1}{2}$ hours it was added to 50.0 g $SiCl_4$ in 100 ml ether with energetic stirring and ice cooling. After 4 hours' boiling, the flask contents were filtered and the ether distilled off. Small amounts of $SiCl_4$ and phenylacetylene were removed by distillation, after which a fraction was isolated in 22.5% yield with b.p. 132-135° at 26 mm.

n_D^{20} 1.5527, d_4^{20} 1.2871, MR_D 58.57; calculated 58.58.
Found %: C 41.53, 41.65; H 2.35, 2.41. $C_8H_5SiCl_3$. Calculated %: C 40.76; H 2.12.

SUMMARY

1. The mechanism of the condensation of R_3SiX with Iotsich's reagent is clarified. It is shown that with rising molecular weight of R in aliphatic liquid R_3SiX, the main reaction is the interaction of R_3SiX with diethyl ether, and the formation of $R_3SiC\equiv CSiR_3$ requires either a large excess of acetylene dimagnesium dibromide or the performance of the condensation in absence of diethyl ether. The compounds $(C_6H_{13})_3SiC\equiv CSi(C_6H_{13})_3$ and $(C_6H_5)_3SiC\equiv CSi(C_6H_5)_3$, were synthesized for the first time. In these compounds the Si−C bond is resistant to hydrolysis by water.

2. It is shown that the Si−C bond in $R_3SiC\equiv CSiR_3$ and $R_3SiC\equiv CR'$ is broken even under mild hydrating conditions (Kucherov's reaction); towards bromine, however, it is very stable, whereas 2 and 4 atoms of bromine can add on at the triple bond.

3. It is established that arylethynyl magnesium halides differ from $XMgC\equiv CMgX$ and $HC\equiv CNa$, in readily condensing with $SiCl_4$.

4. It is established that allylsilanes of the type of $(C=C-C)_X\ SiR_{4-X}$, which are thiocyanated without decomposition, undergo partial beta-decomposition during Kaufmann bromination. Whereas $(C_6H_5)_3SiCH=CH_2$ adds on C_6H_5Li at the double bond without rupture of the Si−C bond, $(C_6H_5)_3SiCH_2CH=CH_2$ undergoes rupture of the silicon−carbon bond under the action of C_6H_5Li with formation of $(C_6H_5)_3SiOH$. A scheme is submitted to account for the high reactivity of the double bond in the beta-position and for the tendency of allylsilanes to break down at the silicon−carbon bond.

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** Evidently a typographical error. No paper by these authors appears on the indicated pages. Publisher.

PREPARATION OF ORGANOVANADIUM COMPOUNDS

V. M. Cherkasov

Like the preparation of any new organoelement compound, undoubted practical and theoretical interest is attached to the preparation of the previously unknown organovanadium compounds with a new type of vanadium-carbon linkage. The literature only mentions a few attempts to prepare organovanadium compounds which did not lead to successful results.

A paper by Vernon [1] mentioned an attempt to obtain organovanadium compounds by reaction of phenylmagnesium bromide with metallic vanadium and with oxides and chlorides of vanadium with various valences.

A.V. Kirsanov and T.V. Sazonova [2] likewise failed to obtain organovanadium compounds from the amyl ester of orthovanadic acid and phenyl magnesium bromide. In both cases the main reaction product was diphenyl, and the formation of organovanadium compounds was only demonstrated by an indirect method; they were not isolated and not analyzed.

The literature also contains a reference to a German patent [3] which describes the preparation of organovanadium compounds by the diazo method. The patent describes experiments on the preparation of double salts from various aryldiazonium chlorides and vanadium pentoxide and the decomposition of these salts with formation of the corresponding organovanadium compounds. The patent omits, however, the reaction equations and the composition of the double diazonium salts and of the organovanadium compounds, since they were not analyzed.

Doubt must be cast upon the possibility in general of preparing such double diazonium salts with vanadium pentoxide, especially since their properties are not described in the patent. Moreover, the decomposition of the double diazonium salts was conducted under conditions excluding the possibility of preparation of organovanadium compounds, namely, heating in an aqueous medium in presence of copper powder, on a water bath. Under such conditions it is natural that the corresponding phenols and vanadium complexes would be formed, or, even more probably, polymeric vanadic acids.

In all the published cases of preparation of organometallic compounds via double diazonium salts, use has been made of double diazonium halides with metallic halides and not with oxides; consequently it would be to the point to attempt to obtain organovanadium compounds by decomposition of double diazonium salts with chlorides of tri- or tetravalent vanadium.

The present work had in view the preparation of the starting double aryldiazonium chlorides with chlorides of vanadium and, in the first place, with vanadium trichloride of the composition $ArN_2Cl \cdot VCl_3$ or $(ArN_2Cl)_2 \cdot VCl_3$.

Bearing in mind the great tendency to hydrolysis of the chlorides of tri-and tetravalent vanadium, we selected one of the variants of the diazo method of A.N. Nesmeyanov [4] – the preparation of double diazonium salts in an anhydrous medium. Dry aniline hydrochloride was diazotized in an alcoholic solution of amyl nitrite. To the precipitated crystalline phenyldiazonium chloride, with cooling, was added an alcohol-ether solution of anhydrous vanadium trichloride.* After separation and washing with dry ether, the salt was obtained in the form of a crystalline, friable, dry substance, highly soluble in alcohol and water, and insoluble in ether. When kept in the air for 1-2 hours, the product appreciably decomposed – at first it turned grey and then brown. When kept overnight in a vacuum desiccator over sulfuric acid or phosphorus pentoxide no appreciable modification of the salt took place.

The substance remains substantially unchanged for several months when kept in a hermetically sealed flask in a refrigerator. When introduced into a flame the salt burns with deflagration like a diazonium salt, and when heated in a flask it decomposes violently at 72-75°. From the analysis for vanadium, chlorine and nitrogen, the salt does not correspond to the expected composition $C_6H_5N_2Cl \cdot VCl_3$ or $(C_6H_5N_2Cl)_2 \cdot VCl_3$. Moreover, titration of the salt solution with ammonium vanadate shows absence of trivalent vanadium. Analyses of the substance correspond to a salt of the composition $(C_6H_5N_2Cl)_2 \cdot VOCl_2 \cdot H_2O$.

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* Anhydrous vanadium trichloride was prepared by a slight modification of the method of [5], starting from vanadium sulfide.

A double diazonium salt is formed in the reaction of phenyldiazonium chloride with vanadium trichloride only after oxidation of the latter to vanadyl chloride $VOCl_2$, which necessitates stirring of the reaction mixture with access of air for 50-60 minutes, and only then is a double salt of the following composition formed:

$$(C_6H_5N_2Cl)_2 \cdot VOCl_2.$$

In confirmation of this conclusion, after addition of a solution containing already prepared vanadyl chloride to the phenyldiazonium chloride, the double salt of phenyldiazonium chloride with vanadyl chloride comes down at once (see Experimental). In a special experiment the possibility was checked of formation of the double salt of phenyldiazonium chloride with vanadium trichloride under conditions excluding oxidation with atmospheric oxygen without access of moisture. The reaction was performed in a stream of dry hydrogen for a period of 2-3 hours; this gave a product with a greyish color which was considerably less stable than the above-described double salt of phenyldiazonium chloride with vanadyl chloride. As a diazonium salt, the substance burns, with violent deflagration; it remains unchanged to outward appearance when kept several hours in a vacuum desiccator. The analytical data for vanadium, chloride and nitrogen in parallel runs deviate by up to 1%, and even to a rough approximation they do not correspond to any of the possible variants of the formulas of the double diazonium salt of phenyldiazonium chloride with vanadium trichloride with varying properties of the two components in the double salt. Evidently a complex salt is formed which contains the diazonium grouping, but its composition could not be established.

Experiments were carried out in addition on the preparation of double salts of vanadium trichloride with aryldiazonium chlorides containing groups in the para-position with an electropositive (CH_3O-) or electronegative ($-NO_2$) character. In the former case the reaction of p-anisyldiazonium chloride with vanadium trichloride led to formation of a salt with the composition $(p\text{-}CH_3OC_6H_4N_2Cl)_2 \cdot VOCl_2$, whose properties resembled those of the double salt of phenyldiazonium chloride and vanadyl chloride. This salt had a brighter green color and likewise changed into a blue hydrate in presence of moisture. The substance possesses much higher thermal stability. Whereas the double salt of vanadyl chloride and phenyldiazonium chloride decomposes with deflagration at 72-75°, the double salt with p-anisyldiazonium chloride does not decompose even when heated on a boiling water bath.

The reaction of p-nitrophenyldiazonium chloride with vanadium trichloride under the same conditions did not lead in general to the formation of a double diazonium salt.

It may be suggested that by choosing appropriate conditions of decomposition, it is possible to obtain, from the prepared double salts of diazonium compound and vanadyl chloride, organovanadium compounds of the composition ArVOCl or Ar_2VO; tetravalent vanadium offers the best possibility of obtaining organovanadium compounds, thanks to its stability toward oxidation.

If it is desired to attempt the preparation of organovanadium compounds with pentavalent vanadium, then evidently double aryldiazonium salts with vanadium oxychloride should be taken for decomposition.

EXPERIMENTAL

Reaction of phenyldiazonium chloride with anhydrous vanadium trichloride. Preparation of the double salt of phenyldiazonium chloride with vanadyl chloride. A solution of 0.01 mole dry aniline hydrochloride (1.3 g) in 6 ml anhydrous alcohol was diazotized at −5 to 0° with 1.5 g (0.013 mole) amyl nitrite. To the phenyldiazonium chloride, a considerable part of which separated in the form of crystals, was added at the same temperature a solution of 0.01 mole anhydrous vanadium trichloride (1.57 g) in 10 ml alcohol and 50 ml anhydrous ether. If the reaction mixture was not stirred, no appreciable change in the precipitate of phenyldiazonium chloride occurred in the course of $1\frac{1}{2}$-2 hours.

Constant stirring of the precipitate caused it to change color and to become more voluminous; after 40-60 minutes the color was light-green and in presence of moisture it gradually acquired a blue tinge. The precipitate was quickly transferred to a filter and washed several times with anhydrous ether. Passage of air through the precipitate should be avoided during its separation since the salt then starts to decompose and to acquire at first a grey and later a brown color. After removal of the ether and drying in a vacuum desiccator the yield was 1.7-1.85 g or about 40-44% for a salt of the composition $(C_6H_5N_2Cl)_2 \cdot VOCl_2 \cdot H_2O$, reckoned on the vanadium trichloride.

The mother liquor, still containing more than 0.005 mole vanadyl chloride, was added to a second portion of phenyldiazonium chloride prepared from 0.01 mole aniline hydrochloride; this led to immediate appearance of a crystalline green or bluish precipitate of double salt in the same yield (40-44%).

If 0.02 mole phenyldiazonium chloride was taken into reaction in one batch with 0.01 mole vanadium trichloride, then the above procedure gave the double salt of phenyldiazonium chloride in one portion with a yield of 80-88%. The properties of the salt have been described above; it should be added that under the ordinary conditions

of working, it is difficult to keep the green-colored salt, which absorbs moisture from the air to form a blue hydrated salt. This occurs in particular when a small sample is taken for analysis, so that the analytical data must be based on the hydrated salt, especially since it is impossible to determine the water content due to the thermal instability of the substance.

Found %: N 13.55, 13.26; Cl 32.24, 32.01; V 11.62, 11.18. $(C_6H_5N_2Cl) \cdot VOCl_2 \cdot H_2O$. Calculated %: N 12.81; Cl 32.44; V 11.66.

For determination of vanadium, a weighed amount was decomposed by heating in concentrated sulfuric acid with a trace of selenium under the conditions of the Kjedahl nitrogen determination. The transparent solution was diluted with water and the vanadium was oxidized to the pentavalent state with excess of permanganate which was destroyed with sodium nitrite. The pentavalent vanadium was then titrated with Mohr's salt in presence of phenylanthranilic acid as indicator.

Reaction of p-anisyldiazonium chloride with vanadium trichloride. Preparation of the double salt of p-anisidyldiazonium chloride with vanadyl chloride. 0.01 mole dry anisidine hydrochloride (1.59 g) was dissolved in 8 ml anhydrous alcohol and diazotized at −5 to 0° with 0.013 mole amyl nitrite (1.5 g). To the solution of diazonium salt, with cooling, was added a solution of 0.005 mole anhydrous vanadium trichloride (0.78 g) in 5-7 ml alcohol and 25 ml ether. A yellowish precipitate was formed which became sticky in the majority of cases. The precipitate was triturated and stirred, and gradually (after 40-50 minutes) became "dry" and friable, and turned light-green. It was collected and washed with dry ether.

Passage of air must be avoided during filtration, otherwise the salt begins to change on the filter. Yield 1.8-2.0 g or about 80% (an additional very small amount of salt is obtained by adding ether to the reaction mixture). The light-green salt absorbs water to form the hydrate with a tinge of blue.

On adding 1-2 drops of water to the reaction mixture, the salt is transformed into the blue hydrate with a tinge of grey. The substance is highly soluble in water, less so in alcohol, and poorly soluble in ether. The salt can be reprecipitated from alcohol with ether. The salt can be kept unchanged in a vacuum desiccator overnight, and for several months in a closed bottle in a refrigerator.

Analysis of the hydrated salt with a light-green color with a bluish tinge.
Found %: N 11.26, 11.45; Cl 28.07, 28.14; V 10.09, 10.41.
$(p\text{-}CH_3OC_6H_4N_2Cl)_2 \cdot VOCl_2 \cdot H_2O$. Calculated %: N 11.27; Cl 28.54; V 10.24.
Analysis of the hydrate of the blue-colored salt formed after addition of water to the reaction mixture.
Found %: N 10.52, 10.80; Cl 27.56, 27.35; V 9.59, 9.73.
$(p\text{-}CH_3OC_6H_4N_2Cl)_2 \cdot VOCl_2 \cdot 2H_2O$. Calculated %: N 10.87; Cl 27.54; V 9.69.

SUMMARY

1. It is shown that on reaction of aryldiazonium chlorides with vanadium trichloride, the oxidation of the latter with atmospheric oxygen results in formation of double diazonium salts with vanadyl chloride.

2. Double salts are obtained of phenyldiazonium chloride and p-anisidyl diazonium chloride with vanadyl chloride of the composition $(C_6H_5N_2Cl)_2 \cdot VOCl_2 \cdot H_2O$ and $(p\text{-}CH_3OC_6H_4N_2Cl)_2 \cdot VOCl_2 \cdot H_2O$.

3. It is shown that introduction of an electropositive substituent (CH_3O) into the para-position of the aryl renders the double salt more stable, while with an electronegative substituent ($-NO_2$) a double diazonium salt is generally not formed.

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Ural Polytechnical Institute

DICHLOROANHYDRIDES OF ALKYLSULFONAMIDOPHOSPHORIC ACIDS

A.V. Kirsanov and N.L. Egorova

On careful hydrolysis of trichlorophosphazosulfonalkyls, as well as on hydrolysis of trichlorophosphazosulfonaryls [1] and tribromophosphazosulfonaryls [2], one atom of halogen is replaced by hydroxyl and dichloroanhydrides of alkylsulfonamidophosphoric acids are formed according to the scheme:

$$AlkSO_2N{=}PCl_3 + H_2O \longrightarrow HCl + AlkSO_2NHPOCl_2.$$

The reaction gives low yields, and the isolation of the dichloroanhydrides of the alkylsulfonamidophosphoric acids in the pure state is extremely difficult, since under the action of water the process barely slows down at the first hydrolysis stage and easily proceeds further.

Dichloroanhydrides of alkylsulfonamidophosphoric acids are more conveniently obtained by the action of anhydrous formic acid according to the scheme:

$$AlkSO_2N{=}PCl_3 + HCOOH \longrightarrow CO + HCl + AlkSO_2NHPOCl_2.$$

The reaction takes place at room temperature with very good yields and nearly quantitatively in all cases.

The dichloroanhydrides of alkylsulfonamidophosphoric acids are colorless and odorless crystalline substances, melting considerably higher than the corresponding trichlorophosphazosulfonalkyls. They are appreciably more stable to atmospheric moisture than the trichlorophosphazosulfonalkyls, and can therefore be easily recrystallized under normal conditions. In the majority of organic solvents the dichloranhydrides of alkysulfonamidophosphroic acids are very much more sparingly soluble than the corresponding trichlorophosphazosulfonalkyls.

The dichloroanhydrides of alkylsulfonamidophosphonic acids react readily with water, alcohols, alkoxides, phenoxides, ammonia, amines and other substances containing active hydrogen atoms, with formation of the corresponding derivatives of alkylsulfonamidophosphoric acids.

EXPERIMENTAL

Preparation of dichloroanhydrides of alkylsulfonamidophosphoric acids. 0.01 mole trichlorophosphazosulfonalkyl is mixed with a solution of 0.01 mole anhydrous formic acid (0.46 g) in 50 ml dry benzene. After 5 minutes carbon monoxide and hydrochloric acid start to come off. The acidolysis is completed by standing at room temperature for 12 hour; the dichloroanhydrides of methyl-, iso-, propyl- and benzylsulfonamidophosphoric acids then separate as well-formed crystals and can be isolated, while the dichloroanhydrides of ethyl-, butyl- and cyclohexylsulfonamidophosphoric acids remain in solution. They are isolated by driving off the solvent in vacuum and recrystallizing the crystalline residue from carbon tetrachloride or ligroin.

Prepared dichloroanhydrides of acids $RSO_2NHPOCl_2$	Yield (%)	Melting point	Found (%)		Calculated (%)	
			Cl	Equivalent after hydrolysis	Cl	Equivalent after hydrolysis
Methylsulfonamidophosphoric $R = CH_3$	98.0	78-81°	32.74 32.87	4.01 4.02	33.45	4.00
Ethyl sulfonamidophosphoric $R = C_2H_5$	96.0	65-68	30.67 30.65	4.03 4.05	31.39	4.00
Isopropylsulfonamidophosphoric $R = C_3H_7$-iso	85.0	114-116	30.15 30.16	3.97 3.97	29.54	4.00
n-Butylsulfonamidophosphoric $R = C_4H_9$-n	88.5	70-72	26.58 26.96	3.98 3.96	27.91	4.00
Benzylsulfonamidophosphoric $R = C_6H_5CH_2$	92.0	123-125	24.98 24.79	4.04 4.04	24.62	4.00
Cyclohexylsulfonamidophosphoric $R = C_6H_{11}$	98.0	90-92	–	3.98	–	4.00

The synthesized compounds are listed in the table.

All the dichloroanhydrides are readily soluble in acetone at room temperature. The ethyl-, butyl- and cyclohexyl-derivatives are also readily soluble in benzene. All the dichloroanhydrides can be recrystallized from ligroine or carbon tetrachloride.

SUMMARY

A study was made of the first stage of acidolysis of trichlorophosphazosulfonalkyls with formic acid. Dichloroanhydrides of alkylsulfonamidophosphoric acids were prepared and described.

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I.V. Stalin Dniepropetrovsk Institute of Metallurgy

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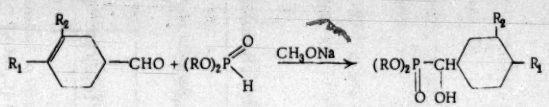
THE INTERACTION OF DIALKYLPHOSPHOROUS ACIDS WITH ALDEHYDES AND KETONES

VIII. ESTERS OF α-HYDROXYCYCLOHEXEN-3-YLMETHYLPHOSPHONIC, α-HYDROXY-(p-METHYLCYCLOHEXEN-3-YL-)-METHYLPHOSPHONIC, AND α-HYDROXY-(3,4-DIMETHYLCYCLOHEXEN-3-YL)-METHYLPHOSPHONIC ACID

V.S. Abramov and A.S. Nazmutdinova

We have previously reported [1] that dialkylphosphorous acids readily add on to the carbonyl group of aldehydes and ketones. The addition reaction proceeds in presence of alkoxides of the alkali metals. A study has been made of the interaction of various dialkylphosphorous acids with aliphatic and aromatic aldehydes and ketones, with alicyclic ketones and with aldehydes of the heterocyclic series [2].

In the present communication we describe the action of dialkylphosphorous acids on 1,2,5,6-tetrahydrobenzaldehyde, p-1,2,5,6-tetrahydrotolualdehyde and 3,4-dimethyl-1,2,5,6-tettahydrobenzaldehyde. The aldehydes were prepared by diene reactions of butadiene, isoprene and dimethylbutadiene with acrolein. The reactions between the specified aldehydes and dialkylphosphorous acids were performed in presence of sodium methoxide and proceeded vigorously with much liberation of heat in accordance with the scheme:



I $R_1 = R_2 = H$;
II $R_1 = CH_3, R_2 = H$;
III $R_1 = R_2 = CH_3$.

The reaction yields substances of relatively high molecular weight which usually, as shown previously [3], undergo decomposition when distilled; we were therefore faced with the problem of finding a convenient and simple method of purification of the prepared esters. In the past the esters of α-hydroxyalkylphosphonic acids were purified by the usual methods of recrystallization and fractional distillation, but in view of the decomposition of the esters when heated, we resorted to a simplified method of purification by absorption of impurities [4], while esters of α-hydroxy-(6-quinolyl)-methylphosphonic acid have been isolated as the picrates [2].

In the present work we took advantage of the difficult solubility of esters of α-hydroxycyclohexen-3-ylmethylphosphonic acid and its homologs in water and of the good solubility of the possible impurities. It was necessary to purify the prepared ester from unreacted tetrahydrobenzaldehyde or its homologs and from the dialkylphosphorous acid, as well as from sodium methoxide. Special experiments showed that the contaminating aldehydes react excellently with sodium bisulfite in aqueous solution and pass into solution. The dialkylphosphorous acids and sodium methoxide were removed with water. These observations were the basis of the following procedure for purification. The product was first washed with an aqueous solution of sodium bisulfite. The separated product was then washed 2 to 3 times with water. Due to the appreciable solubility in water of the methyl and ethyl esters of α-hydroxycyclohexen-3-ylmethylphosphonic acid, these products were washed with saturated sodium chloride solution. The washed product was tested for thoroughness of removal of aldehyde with a solution of fuchsin sulfurous (Schiff's reagent). It should be mentioned that some of the products, for example the butyl and isobutyl esters of α-hydroxycyclohexen-3-ylmethylphosphonic acid, at once gave (even before purification) a negative reaction with fuchsin sulfurous acid. This indicates the definite completion of the reaction. The washed product was dried with fused sodium sulfate and decanted or filtered from it. The filtrate was assumed to be the pure product, on which determinations were made of refractive index, specific gravity and molecular refraction (the latter was compared with the calculated value). Agreement was usually good. This method can be successfully applied also to the separation and purification of other esters of α-hydroxyalkylphosphonic acids, for example in cases [1] when we found that the reactions went, but it proved impossible to separate the product by fractionation.

The esters of α-hydroxycyclohexen-3-yl methylphosphonic acid and its homologs are usually syrupy, colorless, transparent liquids. The isopropyl esthers in all cases are crystalline products which after performance of the reaction

TABLE 1

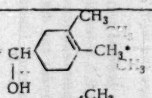
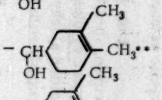
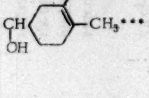
Reactions of dialkylphosphorous acids with 1,2,5,6-tetrahydrobenzaldehyde

Preparation No.	Dialkylphosphorous acids	Weight of reacting substances (in g)		Rise of temperature during reaction period		Formula of prepared compounds	Constants of prepared compounds		MR_D		Content of phosphorus (%)		
		acid	aldehyde	from	to		n_D^{20}	d_4^{20}	Found	Calculated	Found		Calculated
1	$(CH_3O)_2POH$	5.5	5.5	15°	62°	$(CH_3O)_2P(=O)-CH(OH)$	1.4792	1.2200	51.09	51.24	13.28,	13.77	14.09
2	$(C_2H_5O)_2POH$	6.9	5.5	15	62	$(C_2H_5O)_2P(=O)-CH(OH)$	1.4715	1.1544	60.15	60.48	12.66,	12.42	12.50
3	$(iso\text{-}C_3H_7O)_2POH$	3.3	5.5	22	48	$(iso\text{-}C_3H_7O)_2P(=O)-CH(OH)$ *	–	–	–	–	10.81,	11.04	11.23
4	$(C_4H_9O)_2POH$	9.7	5.5	22	64	$(C_4H_9O)_2P(=O)-CH(OH)$	1.4685	1.0816	78.51	78.95	9.99,	10.03	10.19
5	$(iso\text{-}C_4H_9O)_2POH$	9.7	5.5	22	81	$(iso\text{-}C_4H_9O)_2P(=O)-CH(OH)$	1.4668	1.0760	78.39	78.95	10.10,	9.83	10.19

* M.p. 63-64°.

TABLE 3

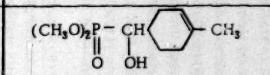
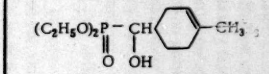
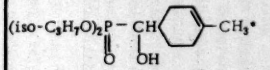
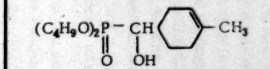
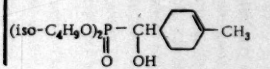
Reactions of dialkylphosphorous acids with 3,4-dimethyl-1,2,5,6-tetrahydrobenzaldehyde

Preparation No.	Dialkylphosphorous acids	Weight of reacting substances (in g)		Rise of temperature during reaction period		Formula of prepared compounds	Constants of prepared compounds		Content of phosphorus (%)		
		acid	aldehyde	from	to		n_D^{20}	d_4^{20}	Found		Calculated
1	$(C_2H_5O)_2POH$	4.9	5.4	20°	96°	$(C_2H_5O_2)P(=O)-CH(OH)$  *	1.4799	1.1270	11.06,	1120	11.23
2	$(iso\text{-}C_3H_7O)_2POH$	5.3	5.0	20	99	$iso\text{-}(C_3H_7O)_2P(=O)-CH(OH)$  **	–	–	10.01,	9.87	10.19
3	$(C_4H_9O)_2POH$	6.4	5.0	20	104	$(C_4H_9O)_2P(=O)-CH(OH)$  ***	–	–	9.25,	9.18	9.34

* MR_D 69.55; Calc. 69.72. ** M.p. 60-62°. *** M.p. 48-50°.

TABLE 2

Reactions of dialkylphosphorous acids with p-1,2, 5,6-tetrahydrotolualdehyde

Preparation No.	Dialkylphosphorous acids	Weight of reacting substances (in g)		Rise of temperature of reaction period		Formula of prepared compounds	Constants of prepared compounds		MR_D		Content of phosphorus (%)		
		acid	aldehyde	from	to		n_D^{20}	d_4^{20}	Found	Calculated	Found		Calculated
1	$(CH_3O)_2POH$	5.5	6.2	15°	76°		1.4875	1.1881	55.72	55.98	12.94,	12.81	13.25
2	$(CH_2H_5O)_2POH$	6.9	6.2	15	77		1.4765	1.1331	65.19	65.21	11.50,	11.69	11.83
3	$(iso\text{-}C_3H_7O)_2POH$	4.2	3.1	21	94		–	–	–	–	10.65,	10.65	10.69
4	$(C_4H_9O)_2POH$	9.7	6.2	14	95		1.4675	1.0566	83.36	83.69	9.72,	9.62	9.75
5	$(iso\text{-}C_4H_9O)_2POH$	9.7	6.2	14	101		1.4722	1.0638	83.72	83.69	9.56,	9.45	9.75

* M.p. 79-80°

or after purification by the above method were filtered, washed, and recrystallized from cyclohexane.

Data for the course of the reactions of dialkylphosphorous acids with the above-mentioned aldehydes and the constants of the prepared esters of α-hydroxycyclohexen-3-ylmethylphosphonic, α-hydroxy-(p-methylcyclohexen-3-yl)-methylphosphonic and α-hydroxy-(3,4-dimethylcyclohexen-3-yl)-methylphosphonic acids are set forth in Tables 1 to 3.

As we see from the data in the tables, our method of purification of the prepared esters of α-hydroxycyclohexen-3-ylmethylphosphonic acids and its homologs gives perfectly satisfactory results and can be extended to other esters. Moreover the reactions of dialkylphosphorous acids with tetrahydrobenzaldehyde and its homologs proceed the more energetically and the more completely the larger the hydrocarbon radical of the dialkylphosphorous acid [5]. This is reflected in the rise in the temperature of the reaction mixture, in the degree of completeness of the reaction (test with fuchsin sulfurous acid) and in the yield of product.

SUMMARY

1. New esters of α-hydroxycyclohexen-3-ylmethylphosphonic, α-hydroxy-(p-methylcyclohexen-3-ylmethyl-phosphonic and α-hydroxy-(3,4-dimethylcyclohexen-3-yl)-methylphosphonic acids were prepared.

2. A simple convenient method of purification of the prepared esters involves washing with sodium bisulfite solution and then with water or sodium chloride solution.

3. It was established that the reaction of dialkylphosphorous acids with tetrahydrobenzaldehyde and its homologs proceeds the more completely the larger the hydrocarbon radical of the dialkylphosphorous acid.

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INVESTIGATION OF THE SOURCES AND ROUTES OF HYDROGEN DURING OXIDATION – REDUCTION REACTIONS

VIII. THE ISOTOPIC EFFECT IN THE CANNIZZARO REACTION •

G.P. Miklukhin and A.F. Rekasheva

With the objective of clarifying the mechanism of the Cannizzaro reaction we have developed a method of synthesis of heavy benzaldehyde C_6H_5CDO and we have determined the magnitude of the isotopic effect during its disproportionation. At the same time we also studied the isotopic effect in the photobromination of heavy toluene.

Benzaldehyde-d_1 was prepared according to the following scheme:

$$C_6H_5CH_2Cl \xrightarrow[2.\ D_2O]{1.\ Mg + ether} C_6H_5CH_2D \xrightarrow{Br_2} C_6H_5CHDBr \xrightarrow{(CH_2)_6N_4} C_6H_5CDO.$$

Methyl-d_1-benzene $C_6H_5CH_2D$ was prepared from benzyl chloride by our previously described method [8]. Even very slow addition of heavy water to the ethereal solution of benzyl magnesium bromide in the reaction flask leads to formation of pellets of magnesium salts, and the heavy water does not react completely. Further hydrolysis of the reaction products must be effected with ordinary water which very seriously dilutes the unreacted water. The resultant toluene contains considerably less deuterium than is calculated from an analysis of the original heavy water. With the objective of improving the utilization of the deuterium, the solution of Grignard compound in ether is conveniently boiled in an apparatus comprising a reaction flask, a bubbler and a reflux condenser, Ether vapor condensing in the condenser enters the lower part of the bubbler which contains heavy water. In rising upwards the ether becomes saturated with heavy water and flows down into the reaction vessel. Reaction with the Grignard compound utilizes the heavy water completely, and only a finely dispersed precipitate of magnesium salts** is formed in the flask. After refractionation over sodium the resultant toluene had b.p. 108.5-109.0°, n_D^{20} 1.4956.

Bromination of heavy toluene was carried out in an apparatus comprising a reactor with a dropping funnel whose end extended to the bottom of the vessel, a reflux condenser cooled with water (for condensation of the small amount of toluene vapor which might be formed during the reaction), and two traps cooled with liquid air. The hydrogen bromide formed during the reaction condensed in the traps. The reaction vessel containing 42 ml heavy toluene was put into a water thermostat in which was inserted a powerful electric lamp. The temperature in the thermostat was kept within the range of 79.9 –80.2°. The amount of bromine brought into reaction (through the dropping funnel) was so adjusted that a specific fraction of the toluene reacted with it. The bromine was added over a period of 15 to 45 minutes depending upon the amount. At the close of the reaction, dry air was blown through the flask contents to remove the dissolved hydrogen bromide. By careful fractionation the residue in the reaction vessel was separated into toluene and benzyl bromide. In different experiments toluene was obtained with n_D^{22} from 1.4950 to 1.4956 and benzyl bromide with n_D^{22} from 1.5747 to 1.5755. Both reaction product and unreacted toluene were burned over copper oxide and the water formed was analyzed for its deuterium content. Results of the experiments are set forth in Table 1.

The ratio of the mean content of deuterium in the methyl hydrogen of the original toluene (A) and of the toluene obtained from the reaction mixture (B) to the content of deuterium in the hydrogen bromide formed (D) in the case of a small amount of reacted toluene is $\frac{\frac{1}{2}(A + B)}{D} = 3.7$. With increasing amount of bromine brought into the reaction the value of this ratio falls, most probably because under these conditions benzylidene bromide is already formed from the benzyl chloride, and the hydrogen in the methyl group of the latter is richer in deuterium than the methyl group in toluene. Extrapolation of the values of $\frac{\frac{1}{2}(A + B)}{D}$ to the instant of start of reaction gives the

• Previous communications in [1-7].

•• This method of synthesis was devloped jointly with I.I. Kukhtenko.

TABLE 1

Bromination of heavy toluene

Toluene reacted (% of original)	Original toulene	Toulene from original mixture		Benzyl bromide		Hydrogen bromide	
	$\Delta d^* \cdot 8$	$\Delta d \cdot 8$		$\Delta d \cdot 7$	$1/2\,(A+B)$	Δd	$1/2\,(A+B)$
	3_A	3_B	A	2_C	C	D	D
25,0	5560	5800	1.04	6250	0.91	1530	3.7
37,5	5560	5820	1.05?	6340	0.90	1665	3.4
50.0	5560	6400	1.15	6600	0.91	—	—
75.0	5560	6950	1.25	6400	0.98?	1930	3.2
87.5	5920	7670	1.30	7370	0.92	2330	2.9

* Δd is the excess density of the waters of combustion in γ.

magnitude of the isotopic effect, i.e. the ratio of the velocities of cleavage of the C—H and C—D bonds equal to 3.8-3.9. The value found for the isotopic effect agrees with the value cited in the literature for the photochlorination of toluene [9].

The ratios of B/A show that under the conditions of bromination of a certain portion of the original toluene, the remaining portion is considerably enriched in deuterium. This is because, due to the isotopic effect, i.e. the lower reactivity of the C—D bond, the molecules of deuterated toluene as a whole are less reactive than the molecules of normal toluene.

Hydrogen bromide is formed preferentially by detachment of hydrogen, and not deuterium, by bromine. The deuterium accumulates in the benzyl bromide. This is illustrated in the fact that during the entire reaction period the value of $\frac{\frac{1}{2}(A+B)}{C}$ remains less than unity.

Heavy benzaldehyde C_6H_5CDO. Samples of benzyl bromide obtained in different experiments were mixed and distilled at 196-200°. A mixture of 24 ml of the prepared benzyl bromide, 29 g urotropine and 250 ml ordinary water was refluxed for 2 hours. The resultant benzaldehyde was distilled off with steam and extracted from the distillate with ether. The bisulfite compound of benzaldehyde, prepared from the ethereal extract by treatment with aqueous sodium bisulfite solution, was washed with ether and decomposed with aqueous sodium carbonate solution. The aldehyde was steam-distilled, extracted with ether and distilled. B.p. 178-179°, $n_D^{19.5}$ 1.5450.

Cannizzaro reaction. Heavy benzaldehyde (20 ml) was vigorously shaken with a solution of 18 g potassium hydroxide in 12 ml ordinary water for 15 minutes. The temperature of the mixture was gradually raised to 80°. During the last 15 minutes, addition was made of 50 ml water, and the cooled mixture was repeatedly extracted with ether. The filtered ethereal layer was vigorously shaken with 50 ml 30% semicarbazide hydrochloride solution and 50 ml 30% potassium acetate. The semicarbazone was filtered off, washed with ether, and dried in vacuum at 100°. Yield 6.2 g. The ethereal solution of benzyl alcohol was dried with sodium sulfate, and after removal of the ether the benzyl alcohol came over at 202-204°. Yield 5.2 g. In a second experiment the benzaldehyde was shaken with KOH solution for 20 minutes. The temperature of the mixture did not exceed 40°. Yield of semicarbazone 11 g; 3 g benzyl alcohol was isolated. In a third experiment from 17 ml benzaldehyde and 18 g KOH in 15 ml water was obtained 17 g semicarbazone and 1.4 g benzyl alcohol. Period of shaking 80 minutes; the temperature did not exceed 30°.

Results of analyses of the waters of combustion of the original benzaldehyde, the benzyl alcohol and of the semicarbazone isolated from the reaction mixture are set forth in Table 2.

The percent migration of deuterium (the isotopic effect), i.e. the ratio of the velocities of cleavage of the C—H and the C—D bonds was determined by us as the ratio of the content of deuterium in the CH_2 group of the benzyl alcohol to its content in the functional group of the original aldehyde. The values of the isotopic effect given in the penultimate column of Table 2 demonstrate that in the Cannizzaro reaction a difference in the velocities of cleavage of the C—H and C—D bonds is experimentally detected only to an insignificant degree. Extrapolation to the instant of commencement of the reaction gives a value of 1.4 for the isotope effect. In an investigation of the disproportionation of benzaldehyde labeled with C^{14} in the functional group, an isotope effect was likewise not detected [10]. The investigation showed that the content of C^{14} in the benzoic acid and in the benzyl alcohol formed during the reaction is the same.

The mechanism of the Cannizzaro reaction has been, and still is, the subject of lively and prolonged discussion.** A free-radical mechanism of this reaction [11] must be rejected in view of the reliable studies of G.I.

* Calculated from the yield of semicarbazone formed from unreacted aldehyde.

** It is remarkable that down to the present day the mechanisms of the Cannizzaro and similar reactions are discussed in the literature without regard to data obtained with the help of isotopes. Thus quite recently a paper was published [16] in which it was suggested that the Cannizzaro reaction goes with intermediate formation of

(footnote continued on following page)

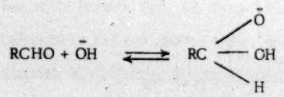
TABLE 2

The isotopic effect in the Cannizzaro reaction

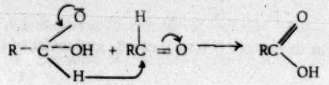
Aldehyde reacted (in %)*	Content of deuterium (in γ)						Percent migration of deuterium	
	In original benzaldehyde		In benzaldehyde		In benzyl alcohol			
			From the reaction mixture					
	In water of combustion of semicarbazone	In carbonyl group A	In water of bombustion of semicarbazone	In carbonyl group C	In water of combustion	In carbonyl group B	From data for alcohol [A/B] · 100	From data for alcohol [C/A] · 100
81	310	2800	390	3500	665	2660	105	125
66	310	2800	410	3690	610	2400	114	132
38	310	2800	350	3120	565	2260	124	112

Kudryavtsev and E.A. Shilova [12] and of M. Kharasch [13]. At all events, such a mechanism is not typical and is realized only under specific conditions and in presence of catalysts of radical reactions.**

The "hydride" mechanism of the Cannizzaro reaction, represented by the following reactions, has found much support in the literature [14]:



(1)



(2)

As we see from these equations, this mechanism implies that the reaction is realized through transfer of negatively charged hydrogen from an ion of the hydrated form of the aldehyde to the non-hydrated form of its molecule. It is known that C−H bonds are broken several times more quickly than C−D bonds [15]; therefore the course of the Cannizzaro reaction according to the mechanism of (1) and (2) ought to have an experimentally detectable and marked isotope effect, since molecules of ordinary benzaldehyde ought to react as hydrogen donors according to equation (2) more rapidly than molecules of the heavy aldehyde.*** If the reaction did not go to completion, the CH_2 groups of the formed benzyl alcohol must contain several times less deuterium than is present in the functional groups of the original benzaldehyde. As we see from the foregoing data, we experimentally established that in the Cannizzaro reaction the ratio of the content of deuterium in the aldehyde to the deuterium content of the alcohol is only a little more than unity.

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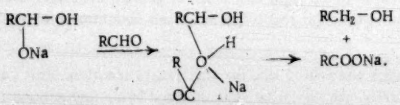
an oxonium compound:



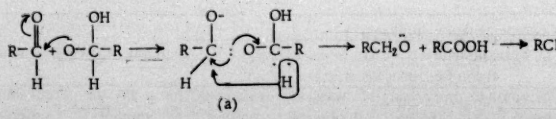
Such an intermediate compound would rapidly exchange the hydrogen linked with oxygen for the deuterium of the water, and deuterium would appear in the C−H bonds of the alcohol if the reaction were conducted in heavy water. This is at variance with data obtained as far back as 1938 [17].

* Calculated from the yield of semicarbazone formed from unreacted aldehyde.

** We previously [6] pointed out that the latent radical reactions to which we relate the Cannizzaro reaction (see below) are very often easily transformed into free-radical reactions.

*** This is true if the reaction rate is governed by the rate of stage (2). In very concentrated caustic alkali solution the reaction of hydration of the aldehyde must actually proceed more quickly. This is confirmed by dependence of the velocity of the Cannizzaro reaction on the square of the concentration.

Our experimental data are in excellent accord with the mechanism of the Cannizzaro reaction put forward as early as 1895 by A.E. Favorsky [18]:

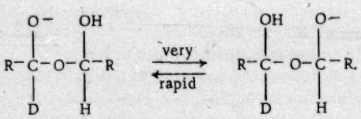


(a)

We believe that cleavage of bonds in the intermediate compound (a) occurs by a homolytic route. There are no grounds for the hypothesis of the translocation of a hydride ion inside compound (a), since there is no positive center in this compound. This mechanism, like the mechanism advanced by Alexander [14], is consistent with the kinetics of the reaction whose velocity depends mostly on the square of the concentration of the aldehyde and primarily on the concentration of base. At the same time, if the reaction proceeds by this mechanism, then a difference in the velocities of cleavage of the C−H and C−D bonds should not be experimentally detected. We shall consider this aspect in more detail.

Intermediate compound (a) may be formed both from two molecules of ordinary aldehyde and from one molecule of ordinary and one molecule of heavy aldehyde. With a small total content of deuterium in the aldehyde (about 3%), formation of compound (a) from two molecules of heavy aldehyde is very improbable.

The intermediate compound of type (a) formed from light and heavy molecules of aldehyde [designated by (b)], is a mixture of two tautomers:



Consequently, independently of whether or not hydrogen or deuterium is translocated, molecules of (b) always form an alcohol containing CHDOH groups.

Thus, both light and heavy benzaldehyde may react in the Cannizzaro reaction with the same velocity, and an isotope effect should not be observed during this process if it goes according to our mechanism.

We are inclined to attribute the slight increase of the percent deuterium transfer over 100%, found by us, to the formation of a small number of molecules of intermediate compound (a) consisting of two heavy molecules of aldehyde. It is natural that the breakdown of such molecules, requiring a high activation energy, should proceed more slowly, and this may explain the small accumulation of deuterium in the unreacted aldehyde. Furthermore, it must be remembered that molecules of (a), formed only from light aldehyde, have the possibility of reacting with cleavage of either of the two C−H bonds, whereas cleavage of molecules of (b) can only be realized at the cost of either one C−H or one C−D bond; hence molecules of (b) will be cleaved slightly more slowly than molecules of (a) which are formed only from light molecules of benzaldehyde.

We previously [1-7] drew attention to the fact that the hydride mechanism of oxidation-reduction reactions of organic compounds is not tenable in the light of a series of general chemical considerations. The experimental data obtained in this investigation support the conclusion that such reactions actually do not go by a mechanism involving the hydride ion.

We suggest that reactions proceeding like the Cannizzaro reaction, with formation of intermediate compounds which break down homolytically, should not be characterized by an appreciable isotope effect. The general validity of this hypothesis, whose value for clarification of the mechanism of chemical processes is obvious, must be checked with reference to a series of other reactions.

SUMMARY

1. The magnitude of the isotope effect was determined in the photobromination of deuterotoluene $C_6H_5CH_2D$ in the liquid phase and in the disproportionation of deuterobenzaldehyde C_6H_5CDO.

2. Unlike what happened in photobromination, when the usual isotope effect was observed (ratio of rates of cleavage of C−H and C−D bonds $K_H : K_D$ = 3.8-3.9), the isotope effect in the Cannizzaro reaction was unusually small ($K_H : K_D = 1.4$).

3. The absence of the normal isotope effect in the Cannizzaro reaction disproves the hypothesis of a bimolecular

reaction mechanism with hydride ion transfer and is consistent with the hypothesis of formation of an intermediate compound of the type of a hemiacetal which undergoes homolytic cleavage.

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THE BISULFITE COMPOUND OF 1 – NAPTHOL.

7 – NITRO – 1 – NAPTHOL

N. N. Karandasheva and S.V. Bogdanov

According to the data of Bucherer [1], 2-hydroxy-1-naphthoic acid, 2-hydroxy-3-naphthoic acid and 1-hydroxy-2-naphthoic acid are converted into the respective napthols on boiling with sodium bisulfite solution. It was noted that decarboxylation of the first two acids gave only 2-naphthol, while in the case of 1-hydroxy-2-naphthoic acid both 1-naphthol and its sulfite are formed. In presence of its sulfite, 1-naphthol is readily soluble and can be isolated only by dilution of the reaction solution with sodium carbonate.

The following reaction scheme was proposed for the case of 2-hydroxy-3-naphthoic acid:

2-Hydroxy-3-napthoic acid → sulfite of 2-hydroxy-3-napthoic acid → 2-naphthyl sulfite → 2-napthol.

On carrying out the reaction of 1-hydroxy-2-naphthoic acid with bisulfite, we found that 1-napthol is abundantly formed during the first hours of the process. On further heating the amount of naphthol diminishes and a homogeneous solution is later formed; a large part of the naphthol (up to 75%) is found to be bound in the form of the bisulfite compound which Bucherer called the "sulfurous ester". In the case of 1-hydroxy-2-naphthoic acid, therefore, the process that takes place is the reverse of that proposed by Bucherer, i.e. the bisulfite compound is not decomposed but the naphthol is converted into the bisulfite compound.

In the present communication we shall not consider the scheme of decarboxylation of 1-hydroxy-2-naphthoic acid and the problem of the structure of the bisulfite compound of 1-naphthol, and shall only examine certain properties of the latter.

The bisulfite compound of 1-naphthol has been very rarely described in the literature. It has been reported [2] that heating of its sodium salt with 1,4-aminophenol hydrochloride to 130-150° in glycerol led to formation of 4'-hydroxyphenyl-1-naphthylamine.

The isolated bisulfite compound of 1-naphthol has the formula $C_{10}H_7OH \cdot NaHSO_3 \cdot H_2O$.

On treatment with ammonia and ammonium sulfite the bisulfite compound is partially converted, even at 60°, into 1-naphthylamine. With caustic alkalies it is readily cleaved into sulfite and naphthol; it is stable in an acid medium. In view of the stability of the bisulfite compound in an acid medium, nitration experiments were undertaken.

Nitration in sulfuric acid solution at −2 to 0° gave a mixture of bisulfite compounds of nitronaphthols. Decomposition of the bisulfite compounds gave a mixture of free nitronaphthols in a yield of 88% of the theoretical, reckoned on the bisulfite compound of 1-naphthol. From the mixture of nitronaphthols were isolated 7-nitro-1-naphthol and a very much smaller quantity of 5-nitro-1-naphthol.

The structure of 7-nitro-1-naphthol was established by oxidation to 4-nitrophthalic acid and by reduction to 7-amino-1-naphthol, while the structure of 5-nitro-1-naphthol was confirmed by comparison with the same compound prepared by a roundabout route.

EXPERIMENTAL

Action of bisulfite on 1-hydroxy-2-naphthoic acid

1. A mixture of 21.0 g (0.01 mole) sodium hydroxynaphthoate and 286 g (1 mole) 36.3% sodium bisulfite solution was boiled 3 hours. The resultant fused 1-naphthol crystallized on cooling. The amount of naphthol separated was 7.0 g (48.6%); needles, m.p. 95.3-95.5°. Further cooling of the solution brought down sodium hydroxynaphthoate, from which 4.65 g free acid was isolated.

2. On prolonging the boiling of the same mixture to 23 hours, a solution was formed with a small sediment of inorganic salts. Dilution of the solution to 500 ml resulted in separation of 1.75 g napthol. The filtrate was acidified with hydrochloric acid, and the liquid with the precipitate was extracted with ether. The ethereal extract was worked up at first with sodium carbonate solution and later with sodium hydroxide. From the sodium carbonate solution was obtained 0.13 g hydroxynaphthoic acid, and from the caustic alkali solution 0.73 g naphthol. The total

quantity of naphthol was 2.48 g (17.2%). The aqueous solution was evaporated down to 300 ml and the bisulfite compound was decomposed by making alkaline with 60 ml 40% sodium hydroxide, heating ½ hour at 70° and acidifying with hydrochloric acid, the amount of 1-naphthol separated was 10.9 g (75.7%).

Bisulfite compound of 1-naphthol

A mixture of 10.5 g sodium 1-hydroxy-2-naphthoate with 143 g 36.3% bisulfite solution was boiled 23 hours. The residue of hydroxynaphthoic acid and naphthol was removed as described above; the solution after partial neutralization with sodium carbonate was evaporated to a volume of 150 ml and cooled to 7°. The precipitate of bisulfite compound (rhombic platelets) was filtered and washed with alcohol; yield 8.73 g (0.93 g naphthol) was separated from the filtrate by decomposition of the residue of bisulfite compound).

Colorless needles (from aqueous alcohol), very easily soluble in water, sparingly in alcohol.

For iodometric analysis of the bisulfite compound, a weighed sample was dissolved in 25 ml water, the solution was made alkaline with 5 ml 40% sodium hydroxide, and after stadding 15 minutes at room temperature it was diluted with 1500 ml water, acidified with hydrochloric acid and titrated with iodine.

1.072 g substance: loss on drying (120°) 0.0752 g. 0.3060 g substance: 0.0814 g Na_2SO_4. 0.3001 g substance: 22.39 ml 0.1 N I_2. Found %: H_2O 6.79; Na 8.61. M 268.0. $C_{10}H_9O_4SNa \cdot H_2O$. Calculated %: H_2O 6.77; Na 8.64. M 266.2.

1-Naphthylamine

A mixture of 24.8 g (0.093 mole) bisulfite compound of 1-naphthol, 35 ml ammonium bisulfite solution containing 21 g (0.33 mole) SO_2, and 45 g (0.78 mole) 29.7% ammonia was kept at 60° for 20 hours. Two layers were formed; the upper one crystallized on cooling. Amount of solid 11.65 g, m.p. 53.2-58.0°.

The filtrate was extracted with benzene, then treated with sodium hydroxide, acidified with hydrochloric acid and again extracted with benzene. The main precipitate proved to be a mixture of naphthylamine and naphthol.* 2.260 g of the mixture was treated with dilute hydrochloric acid, and the mixture extracted with benzene. Diazotization of the aqueous solution required 17.45 ml 0.5 N $NaNO_2$ (a). Coupling of the solution of diazo compound by Grachev's method [3] required 87.35 ml 0.1 N solution of 1-(4'-sulfophenyl)-3-methyl-5-pyrazolone (b). Amount of 1-naphthylamine found, reckoned on 11.65 g mixture: (a) 6.43 g; (b) 6.44 g (48.4%).

From the benzene extract was separated 0.956 g 1-naphthol; total quantity of naphthol in mixture 4.93 g.

On carrying out the reaction with ammonia in the absence of ammonium sulfite, the yield of 1-naphthylamine after 6 hours was 12%.

Nitration of the bisulfite compound

53.2 g (0.2 mole) bisulfite compound at 3-5° was gradually introduced into 300 ml chemically pure sulfuric acid. To the colorless solution at −2 to 0° was added in the course of 1½ hours a mixture of 8.8 ml (0.204 mole) 97% nitric acid and 60 ml sulfuric acid, and stirring at this temperature was continued for 2 hours. The light-brown mass was run into a mixture of water and ice, the resultant solution was neutralized with chalk, and the calcium sulfate was filtered off and washed with hot water; the orange-colored filtrate was concentrated to a volume of 1250 ml.

Part of the solution was heated with iron filings and a small quantity of acetic acid; the iron was precipitated with sodium carbonate and the filtrate diazotized. With 2-naphthol the diazo compound gave a reddish-orange solution which did not change on acidification with hydrochloric acid. On addition of sodium hydroxide, the color changed to dark-red, and on further acidification a reddish-brown precipitate came down. The solution obtained by coupling the diazo compound with resorcinol had similar properties. On further evaporation of part of the solution, the bisulfite compound of nitronaphthol could not be isolated in the crystalline form. After evaporation to dryness, the residue was treated with 90% alcohol; concentration of the alcoholic solution gave a non-crystallizing, viscous, brown mass.

To 938 ml solution of bisulfite compound of nitronaphthol was added 75 ml 35% sodium hydroxide solution; a rich cherry-red color was developed, and red needles of the sodium salt of nitronaphthol came down. The mixture was kept 15 minutes at 50-60° and acidified with sulfuric acid; sulfur dioxide was evolved, and free nitronaphthol came down (orange needles). The precipitate was filtered and washed with water; weight 29.9 g, m.p. 195-200°. Extraction of the filtrate with ether yielded 1.13 g nitronhaphthol with m.p. 150-160° and 0.22 g 1-naphthol.

The main precipitate of nitronaphthol was treated several times with boiling dichloroethane until the color of the solution was weak, and after that with hot nitric acid; 5.0 g insoluble residue (gypsum) was obtained. Yield of nitronaphthol on basis of original volume of solution 33.2 g (87.8%).

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* From the benzene solutions was obtained 0.1 g of a mixture of naphthol and naphthylamine and 0.36 g naphthol.

From the acetic acid solution was separated 15.1 g nitronaphthol with m.p. 205-210°, while the dichloroethane solution gave 8.4 g with m.p. 140-147°. Repeated recrystallization of the low-melting nitronaphthol from dichloroethane, aqueous methanol and water gave 3.7 g nitronaphthol with m.p. 197-209° and 3.2 g nitronaphthol with m.p. 151-159°. This mixture contained a minute amount of 1-naphthol. The total quantity of nitronaphthol with a high melting point was 76% of the total of isomers.

7-Nitro-1-naphthol

It was obtained by successive recrystallizations of the nitronaphthol with m.p. 197-210° from acetic acid and dilute methanol. Yellow needles (from aqueous methanol or water), m.p. 213.8-214.5°. Fairly highly soluble in ether, with more difficulty in benzene, acetic acid and alcohol; sparingly soluble in water. The sodium carbonate solution had a red color.

4.370 mg substance: 10.098 mg CO_2; 1.480 mg H_2O. 3.316 mg substance: 0.231 ml N_2 (35°, 722 mm). Found %: C 63.01; H 3.79; N 7.34. $C_{10}H_7O_3N$. Calculated %: C 63.49; H 3.73; N 7.40.

4-Nitrophthalic acid. A solution of 1.9 g 7-nitro-1-naphthol, 0.5 g potassium permanganate and 0.5 g potassium hydroxide in 175 ml water was boiled until decolorized (3 hours) and filtered. The filtrate was acidified with sulfuric acid and evaporated to dryness. Ether extraction of the residue yielded 1.45 g nitrophthalic acid. Yellow needles (from ether), m.p. 161-161.5°.

7-Amino-1-naphthol. A solution of 1.9 g nitronaphthol in 50 ml methyl alcohol was gradually run into a heated mixture of 3 g iron filings and 7 ml water, acidified with hydrochloric acid, and the mixture boiled 30 minutes. The hot mixture was made alkaline with sodium hydroxide and filtered. The aminonaphthol was isolated by acidifying the filtrate with hydrochloric acid until acid to litmus; yield 1.4 g.

Rectangular and hexagonal colorless platelets (from water), m.p 154.5-155° (with decomp.). The literature [4] gives m.p. 155-156°.

The N-acetyl derivative. Prepared by treating aminonaphthol with boiling acetic anhydride, and purified by reprecipitation from sodium hydroxide solution. Colorless platelets, m.p. 220-221° (with decomp.).

5-Nitro-1-naphthol

Prepared by alternate extraction of nitronaphthol with m.p. 151-159° with small quantities of boiling dichloroethane and water. The fraction with m.p. 165-168°, separated from the solutions, was recrystallized from dichloroethane and water. Long yellow needles (from water), m.p. 171.5-172°. Considerably more soluble in organic solvents and water than the isomeric nitronaphthol. Sodium carbonate solution colored red.

The comparison preparation of 5-nitro-1-naphthol was obtained by the method of N. Vorozhtsov and A. Kulev [5] by reduction of 1,5-dinitronaphthalene with a mixture of sodium sulfide and ammonium sulfate to 5-nitro-1-naphthylamine, diazotization of the latter, and decomposition of the diazo compound. M.p. 172-172.5°. The mixture of nitronaphthols melted at 172-172.5°.

SUMMARY

1. Decarboxylation of 1-hydroxy-2-naphthoic acid with sodium bisulfite gives at first 1-naphthol, and then the bisulfite compound of 1-naphthol.

2. Treatment of the bisulfite compound of 1-naphthol with ammonium sulfite and ammonia at 60° converts it into 1-naphthylamine.

3. Nitration of the bisulfite compound of 1-naphthol in sulfuric acid solution leads to the bisulfite compounds of 7-nitro- and 5-nitro-1-naphthols.

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K.E. Voroshilov Research Institute for Organic Intermediates and Dyes

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AMINOTRIARYLCARBINOLS

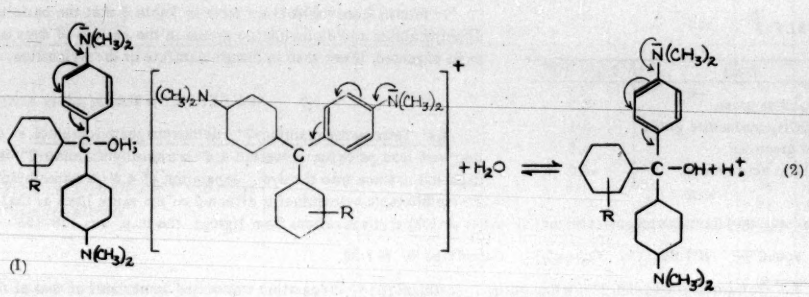
O.F. Ginzburg and N.S. Melnikova

Derivatives of triarylcarbinols containing amino groups in the para position to the central carbon atom are capable of dissociating in various solvents, including water, according to the equation

$$\equiv C-OH \rightleftharpoons [\equiv C^{+}] + OH^{-}. \qquad (1)$$

For the purpose of comparing the influence exerted by electron donating and electron accepting groups on the dissociation of aminotriaryl carbinols in accordance with equation (1), determinations were made of the dissociation constants of some derivates of 4,4'-tetramethyldiaminotriphenylcarbinols possessing the general formula (I).

Calculation of the dissociation constants of aminotriarylcarbinols was performed on the basis of experimental data obtained in a quantitative study of the equilibrium represented by equation (2), in solutions prepared by addition to various buffered mixtures of aminotriarylcarbinols or of the dyes formed from them.



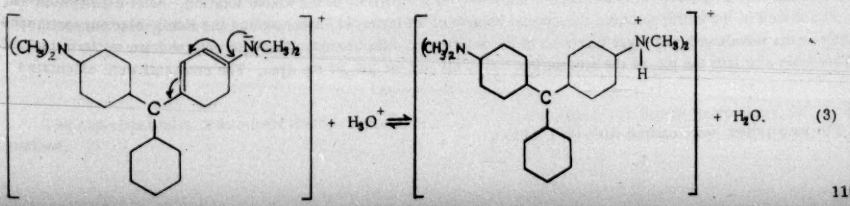
The values found for the dissociation constants (at 17 ± 1°) are listed in Table 1.

TABLE 1

Compound	K_d
4,4'-Tetramethyldiaminotriphenylcarbinol	$5.9 \cdot 10^{-8}$
4,4'-Tetramethyldiamino-2"-methoxytriphenylcarbinol	$1.9 \cdot 10^{-7}$
4,4'-Tetramethyldiamino-3"-methoxyphenylcarbinol	$6.3 \cdot 10^{-8}$
4,4'-Tetramethyldiamino-4"-nitrotriphenylcarbinol	$2.8 \cdot 10^{-9}$
4,4'-Tetramethyldiamino-3"-nitrotriphenylcarbinol	$4.4 \cdot 10^{-9}$
4,4'4"-Hexamethyltriaminotriphenylcarbinol	$3.2 \cdot 10^{-5}$

The values of the dissociation constants of 4,4'-tetramethyldiaminotriphenylcarbinol and 4,4',4"-hexamethyltriaminotriphenylcarbinol given in Table 1 are in very excellent agreement with the values of these constants calculated from the pH values of aqueous solutions of the dyes formed from these aminotriaryl carbinols [1].

Change of color of solutions of triarylmethane dyes is observed, as we know, not only under the action of alkalies but also under the influence of acids. The action of acids is based upon the addition of protons to the amino groups, due to which the electron-donating substituents are transformed into electron acceptors, and an equilibrium is set up in the solution which, for example in the case of malachite green, may be represented by equation (3)



Quantitative study of the above equilibrium permits determination both of the hydrolysis constant of the doubly charged ion (the second hydrolysis contant K'_1) and the associated basicity constant of the dimethylamino group in the singly charged ion– the cation of the dye K_0. Since transformation of the singly charged cation into the doubly charged one is accompanied by a marked deepening of color, it is possible to evaluate the change of concentration of the singly charged ion in solution from the change in the value of the optical density of the solution at a wavelength close to γ_{max} of malachite green. By means of the colorimetric method, determinations were made of the concentration of singly charged ion in solutions of malachite green possessing a low pH, and on the basis of these data the second hydrolysis constant of malachite green was determined and found to be equal to $2.52 \cdot 10^{-3}$ (17°). A similar value for the second hydrolysis constant of malachite green is obtained from a treatment of the experimental data in Henriques' paper [2]. On the other hand a value of the second hydrolysis constant of malahcite green which is nearly 30 times higher than the above value is given in a paper by Schwarzenbach and co-workers [3]. In this connection attention should be drawn to an error in Schwarzenbach's work. In the determination of the concentration of the singly charged cation Schwarzenbach compared the optical density of the investigated solutions with the optical density of malachite green solution with a pH of 7; in their calculations the authors did not take account of the fact that more than half of the dye present in such a solution is converted into colorless carbinol.

As was noted above, a quantitative study of the equilibrium represented by equation (3) permits determination not only of the second hydrolysis constant of the doubly charged ion but also of the basicity constant of the amino group in the cation of the dye K_0^+. In Table 2 is listed the basicity constant of the dimethylamino group in the cation of malachite green, and also that in the cation of the dye formed from 4,4'-tetramethyldiamino-3'-methoxytriphenylcarbinol (m-OCH_3-malachite green). In the same table are included the constants characterizing the basicity of the diethylamino group in the dyes Acid green Zh and Brilliant acid Blue Z (at 17 ± 1°).

TABLE 2

Dyes	$K'_0 \cdot 10^{12}$
Malachite green	2.9
m-OCH_3-malachite green	3.1
Acid green Zh	5.6
Brilliant acid blue Z	4.0

It follows from the data set forth in Table 2 that the basicity of the dimethylamino and diethylamino groups in the cations of dyes is, as was to be expected, lower than in dimethylaniline or diethylaniline.

EXPERIMENTAL

4,4'-Tetramethyldiamino-2"-methoxytriphenylcarbinol.* Oxidation with lead peroxide converted 4,4'-tetramethyldiamino-2"-methoxytriphenylmethane into the dye. Separation of 4,4'-tetramethyldiamino-2"-methoxtriphenylcarbinol is effected on the same lines as that of 4,4'-tetramethyldiaminotriphenylcarbinol [4]. After several crystallizations from ligroin the m.p. was 156-158°.

Found %: N 7.68, 7.72. $C_{24}H_{28}O_2N_2$. Calculated %: N 7.64.

4,4'-Tetramethyldiamino-3"-methoxytriphenylcarbinol [6]*. Preparation was on the same lines as that of the above carbinol. M.p. 139-140° after several crystallizations from ligroin.

Found %: N 7.61, 7.65. $C_{24}H_{28}O_2N_2$. Calculated %: N 7.46.

Picrate of 4,4'-tetramethyldiamino-4"-nitrotriphenylcarbinol. Preparation as described in the literature [5]. Crystallized twice from alcohol.

Found %: N 13.94. $C_{23}H_{24}O_2N_3 \cdot C_6H_2O_7N_3$. Calculated %: N 13.96.

Picrate of 4,4'-tetramethyldiamino-3"-nitrotriphenylcarbinol. Preparation as described in the literature [5]. Twice crystallized from alcohol.

Found %: N 13.96, 14.25. $C_{23}H_{24}O_2N_3 \cdot C_6H_2O_7N_3$. Calculated %: N 13.96.

The picrate of malachite green and the hydrochloride of crystal violet were prepared from the carbinol compounds obtained in the chemically pure form. The dyes Acid green Zh and Brilliant acid blue Z were taken in the form of commercial samples.

Determination of dissociation constants of aminotriarylcarbinols

10^{-4} mole of carbonyl compound or dye was dissolved in 100 ml acetone or the same amount of water. To 25.0 ml buffer solution with a different pH was added a few tenths of a milliliter of the above solution. After equilibrium had been established in the buffer solution, the optical density of the latter was measured on the König-Martens spectrophotometer at the wavelength and layer thickness of the solution specified below. The data obtained are set forth in Table 3. This table also lists the pK_0 of the aminotriarylcarbinols and the pK_h of the dyes. The constants were calculated

* The preparations were carried out with I. Mishina.

from equations (4) and (5):

$$pK_0 = pK_w - pK_h, \tag{4}$$

$$pK_h = pH - \log \frac{1-a}{a}; \quad a = \frac{E}{E_{max}}, \tag{5}$$

where E is the magnitude of the optical density of the solution examined, and E_{max} is the value of the optical density of a solution in which the equilibrium expressed by equation (2) is substantially completely shifted to the left; in other words E_{max} characterizes the optical density of a solution of dye in which hydrolysis of the latter is suppressed. Values of E_{max} were determined either experimentally or by calculation by the method of least squares or by equation (6).

$$E_{max} = \frac{E'E''(1-n)}{E'' - nE''}, \tag{6}$$

where $n = \frac{[H^+]''}{[H^+]'}$.

In Table 3 the calculated value of E_{max} (17 ± 1°), is marked with an asterisk.

TABLE 3

Compound	Amount of dye (in ml)	Thickness of layer (in mm)	λ (mμ)	pH	E	E_{max}	pK_0	pK_h
Malachite green picrate	0.1	20	620	4.01	0.688	0.688	–	–
				6.92	0.360		7.21	6.96
				7.10	0.280		7.23	6.94
				7.70	0.101		7.25	6.92
4,4'-Tetramethyldiamino-3"-methoxytriphenylcarbinol	0.1	50	620	6.36	0.892	1.060*	7.19	6.98
				6.90	0.536		7.26	6.91
				7.12	0.442		7.21	6.96
				7.36	0.311		7.14	7.03
4,4'-Tetramethyldiamino-2"-methoxytriphenylcarbinol	0.1	50	620	4.01	0.580	0.580	–	–
				6.90	0.445		6.76	7.41
				7.12	0.402		6.70	7.47
				7.36	0.335		6.68	7.49
4,4'-Tetramethyldiamino-4"-nitrotriphenylcarbinol picrate	0.1	50	640	3.90	0.736	0.736	–	–
				5.00	0.592		8.55	5.62
				5.90	0.237		8.59	5.58
				6.36	0.113		8.55	5.62
4,4'-Tetramethyldiamino-3"-nitrotriphenyl carbinol picrate	0.2	50	620	3.90	1.057	1.057	–	–
				5.90	0.456		8.39	5.78
				6.00	0.403		8.38	5.79
				6.34	0.258		8.32	5.85
Crystal violet	0.1	50	590	3.90	0.785	0.785	–	–
				9.54	0.447		4.51	9.66
				9.90	0.290		4.48	9.69

Determination of basicity of amino groups in cationic dyes

The procedure for determination was similar to that described above. Results of measurements are listed in Table 4. Values of pK'_h were determined in accordance with equation (7)

$$pK'_h = pH - \log \frac{a}{1-a}. \tag{7}$$

The experimentally determined values of E_{max} (17 ± 1°), given in Table 4 can also be found by the calculative method.

TABLE 4

Compound	Amount of dye (in ml)	Thickness of layer (in mm)	λ (mμ)	pH	E	E_{max}	pK'_0	pK_h
Malachite green picrate	0.1	20	620	1.57	0.053	0.688	11.54	2.63
				2.05	0.130		11.49	2.68
				3.04	0.498		11.54	2.63
				3.07	0.538		11.60	2.57
4,4'-Tetramethyldiamino-3"-methoxytriphenylcarbinol	0.1	50	620	1.6	0.080	1.060	11.5	2.7
				3.0	0.690		11.5	2.7
Acid green Zh	0.3	50	640	6.98	0.658	0.658	–	–
				3.40	0.496		11.25	2.92
				3.10	0.393		11.24	2.93
				2.70	0.250		11.25	2.92
Brilliant acid blue Z	0.3	20	630	8.10	1.656	1.656	–	–
				3.40	1.329		11.38	2.79
				3.10	1.103		11.37	2.80
				2.70	0.810		11.45	2.72
				2.13	0.318		11.42	2.75

SUMMARY

1. A study was made of the dissociation constants of six triarylcarbinols containing electron-donating and electron-accepting substituents.

2. It was shown that the basicity of dimethylamino- and diethylamino groups in cations of triarylmethane dyes is very much lower than the basicity of dimethylaniline or diethylaniline.

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Leningrad Lensoviet Institute of Technology

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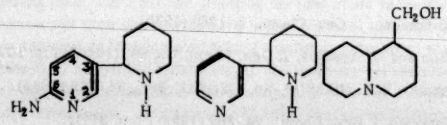
METHOD OF PREPARATION OF 6-AMINOANABASINE AND LUPININE FROM A COMMERICAL MIXTURE OF ANABASINE AND LUPININE

N.V. Khromov-Borisov and E.G. Vatkina

6-Aminoanabasine (I) is prepared from anabasine (II) and sodium amide by the Chichibabin reaction [1-4]. Preparation of this compound is a complex operation because in the course of separation of pure anabasine from the natural mixture of alkaloids we have to deal with a fraction consisting of anabasine (II) and lupinine (III) [5]. To separate anabasine from lupinine, however, without application of chemical methods is practically impossible.



(I) (II) (III)

Between 1931 and the present day, various Soviet chemists have proposed a whole series of methods of resolving mixtures of anabasine and lupinine.

Thus, A.P. Orekhov proposed methods of resolution by benzoylation and nitrosation [5, 6]. S.A. Zaboev later modified the method of nitrosation and suggested conducting the reaction in acetic acid [7]. A. Sokolov effected the separation with the help of hydrofluosilicic acid [8]. A.S. Sadykov and G.V. Lazurevsky proposed to effect separation of the mixture with the help of metallic sodium [9]. This method was later modified by Sadykov and Spasokukotsky who replaced metallic sodium by sodium amide in liquid ammonia [10]. A.S. Sadykov and O. Otroshchenko put forward the hydrochloride method for separation of a mixture of anabasine and lupinine [11]. V.V. Udovenko, O.I. Granitova and L.A. Vvedenskaya developed the method of formation of copper-anabasine complex compounds for resolution of a mixture of anabasine and lupinine [12].

Opinion is divided as to which of these methods is to be preferred. Various authors have published conflicting evaluations [5, 11].

We have found that 6-aminoanabasine can be successfully prepared by the action of sodium amide on the unresolved commercial mixture of anabasine and lupinine [13]. In this reaction the anabasine is converted into aminoanabasine while the lupinine forms sodium lupinate, which after treatment of the reaction mixture with water is again split up into lupinine and sodium hydroxide. Our experiments showed that the presence of lupinine not only does not interfere, but even facilitates a successful course of the reaction: the amount of resin formed is reduced and the yield of aminoanabasine increases $1\frac{1}{2}$-2 times. No difficulty is met in the separation of pure 6-aminoanabasine and lupinine since their boiling points differ widely: lupinine comes over at 125-128° (7 mm) and aminoanabasine at 185-195° (7 mm).

Aminoanabasine is obtained in 41% yield reckoned on the anabasine entering into reaction; under similar conditions pure anabasine (not containing lupinine) forms 6-aminoanabasine in a yield of 22-29%.

EXPERIMENTAL

In a round-bottomed flask fitted with reflux condenser (and calcium chloride tube) and stirrer with mercury seal are placed 50 g of a mixture of alkaloids, containing 80% anabasine and 20% lupinine, 30 g thoroughly pulverized sodium amide and 300 g freshly distilled dimethylaniline. The mixture is heated with stirring on an oil bath for 11 hours: the first 5 hours at 130-135° and 6 hours at 140-145°. At the end of the reaction the mixture is decomposed with iced water and extracted with ether. The ethereal solution is dried with ignited potassium carbonate, the ether is taken off, and the residue subjected to vacuum distillation: 1st fraction, b.p. to 100° at 7 mm (approx. 300 g) con-

tains dimethylaniline; 2nd fraction, b.p. 125-128° at 7 mm (10.6 g) contains lupinine and unreacted anabasine. This mixture crystallizes on shaking. From it was isolated 6.8 g lupinine and 3.8 g anabasine. The 3rd fraction, b.p. 185-195° (7 mm) contains aminoanabasine and lupinine; total weight 18.2 g. Recrystallization of this fraction from toluene gives 16.0 (40.5%) aminoanabasine (m.p. 109°); the toluene mother liquor yielded 2 g lupinine. Total amount of lupinine 8.8 g (88%), m.p. 68°. In addition 11 g resinous still residue is obtained.

SUMMARY

A method is proposed for amination of an unresolved mixture of anabasine and lupinine with the help of sodium amide.

It was established that the presence of lupinine does not interfere with the amination of anabasine and even facilitates the reaction and brings about an improved yield. 6-Aminoanabasine is formed in 40.5% yield. In addition lupinine is isolated in pure form in 88% yield.

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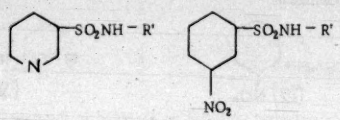
THE ANALOGY BETWEEN CERTAIN PROPERTIES OF DERIVATIVES OF β-PYRIDINESULFAMIDE AND m-NITROBENZENESULFAMIDE

E.Yu. Tsekhanovich, I.Ya. Postovsky and V.F. Degtyarev

Many of the compounds belonging to the great class of sulfamides are known to exhibit antibacterial properties. We undertook the synthesis of a hitherto neglected type of sulfamides – derivatives of β-pyridinesulfonic acid. These compounds presented interest as possible biological antagonists of nicotinic acid – a compound important for the metabolism of macroorganisms and some microorganisms. In addition we thought it would be interesting to compare the properties of β-pyridinesulfamides with the properties of m-nitrobenzenesulfamides. In nitration, sulfonation and halogenation reactions, the nitrogen of the pyridine ring exercises an influence similar to that of the nitro group in nitrobenzene, hindering these reactions and directing the substituent to the β-position. Several other reactions of pyridine and nitrobenzene and their derivatives have been described [1, 2], and these point to a "similarity" of these compounds which is assumed to be associated with a similar distribution of electron density in their molecules [3]. Apart from the synthesis of β-pyridinesulfamides (I), the synthesis was therefore effected of several m-nitrobenzenesulfamides (II). For the characterization of these compounds from the viewpoint of the above-mentioned analogy, the values of their acidic dissociation constants (or $pK_a = -\log K$) may be informative.



(I) (II)

Sulfamido compounds dissolve in caustic alkali due to the acidic hydrogen of the sulfamido group. In appropriate solutions they can dissociate according to the equation

$$R - SO_2NH - R \rightleftharpoons [R - SO_2N - R']^- + H^+.$$

The acidity of sulfamides depends, however, on the chemical character of the radicals R and R', i.e. on the structure of the molecule as a whole, and consequently the change of the acidic dissociation constants is a convenient method of characterizing the properties and structural features of sulfamides.

The sulfamido compounds described here (Table 5) were prepared by condensation of the acid chlorides of sulfonic acids with the appropriate amines according to the equation

$$R - SO_2 - Cl + R' - NH_2 \rightarrow R - SO_2NH - R' + HCl.$$

Some of the preparations, mainly derivatives of β-pyridinesulfamide, have not been described in the literature. Analytical data and general characteristics are given for these compounds.

Results of determination of the acidic dissociation constants are given in the form of pK_a. Table 1 gives the acidity of phenylsulfamides of three different types: N-phenylbenzenesulfamide (compound 1), β-(N-phenyl)-pyridinesulfamide (compound 2) and N-phenyl-m-nitrobenzenesulfamide (compound 3). As we see from the data of Table 1, introduction of a nitro group and replacement of the benzene ring by the pyridine ring raise the acidity; in this connection it should be mentioned that in both these cases pK_a changes to an identical extent.

The data of Table 2 show that the nitro group introduced into the N-phenyl ring of compounds 2 and 3 considerably raises the acidity of sulfamides, and most appreciably when present in the ortho- and para-positions of the phenyl radical. Replacement of the N-phenyl radical as a whole by a pyridine residue linked with the sulfamido group in the α-position also increases the acidity. The quantitative agreement between the values of pK_a for the compounds of both types is noteworthy.

Judging by the data of Table 3, an atom of chlorine introduced into the N-phenyl also increases the acidity of

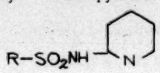
TABLE 1

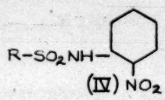
Compound Number	Sulfamides: R – SO_2NH –	pKa
	R	
1		10.80*
2		9.60
3		9.55

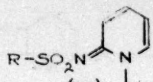
sulfamides, although to a lesser degree than the nitro group. The dependence of the acidity on the position of the substituent is here again different. The acidity is highest in the case of sulfamides whose chlorine atom is in the ortho-position to the phenyl, less high when the chlorine is in the meta-position, and lowest when the chlorine is the para-position. Here, as with the compounds listed in Table 2, there is close agreement of the values of pK_a of the corresponding derivatives of β-pyridinesulfamide and m-nitrobenzenesulfamide.

In Table 4 is illustrated the influence of a methoxyl group upon the acidity of sulfamides of the same types: sulfamides containing a methoxyl group have a lower acidity than the unsubstituted compounds. The rise of acidity of sulfamides under the influence of electron-accepting groups such as the nitro group and the chlorine atom, and conversely the reduction in acidity by electron-donating groups such as methoxyl are consistent with other literature data [4, 5] on the change of dissociation constants of organic compounds in dependence on structure.

The data illustrate the quantitative agreement between the pK_a values of corresponding derivatives of β-pyridinesulfamide and m-nitrobenzenesulfamide. This agreement confirms in some measure the above-mentioned "similarity" between pyridine and nitrobenzene.


(III)


(IV)


(V)

It may be suggested that such a "similarity" will also be observed in the case of compounds of the type of (III) and (IV). In fact, however, the acidity of compounds of the indicated structure, containing a pyridine ring (III), is lower than that of the corresponding compounds with a nitro group (IV) in the orthoposition of the benzene ring (compare in Table 2 compounds 6 and 10, 9 and 11). This is evidently associated with the possibility of formation to some extent of the tautomeric imino form (V) in the case of compounds (III) under the reaction conditions. This tautomer may influence the value of the dissociation constant in the direction of its reduction (the hydrogen attached to the nitrogen of the pyridine ring possesses no acidic properties).

EXPERIMENTAL

Determination of acid dissociation constants of the synthesized compounds was effected by potentiometric titration using a quinhydrone electrode in a Moskip-4 potentiometer and with a glass electrode in a lamp pH-meter. Due to the very slight solubility of the majority of sulfamides in water, 96% alcohol was used as the solvent. Use of an alcoholic medium as the solvent generally permits determination, with good reproducibility, of the pK_a of compounds with values up to 9. The acid dissociation constants of sulfamides, as weak electrolytes, was calculated graphically by finding the pH of the solution at the point of half neutralization of the compound.

The acidity of sulfamides in an alcoholic medium in general is considerably lower than their acidity in an aqueous medium. We could evaluate the difference by comparing the values of the dissociation constants of some compounds in an aqueous and in an alcoholic medium. For example, the pK_a of N-acetylsulfamide, measured by us in an aqueous medium, is 5.95, in agreement with the literature [5], whereas in an alcoholic medium the pK_a is 7.35. This order of influence of the solvent on the pK_a had already been reported in the literature [10-12]. We present several curves of potentiometric titration of the individual sulfamides.

Preparation of β-pyridinesulfonic acid. The preparation was effected by a slight modification of McIlwain's method [13], the change consisting in the use of a slightly higher sulfonation temperature (260-265° instead of 240°) and a simpler procedure for separation of the prepared product. Instead of the recommended vacuum distillation of the excess sulfuric acid, the compound was at once precipitated with methyl alcohol after conclusion of the sulfonation reaction and cooling to 0°. The sulfonic acid then comes down at once in the pure state in the form of pale-cream crystals. By these modifications the duration of the synthesis could be cut and the yield raised to 75%.

* The value of pK_a is rounded off to the second decimal place.

TABLE 2

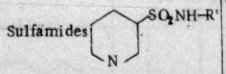
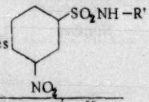
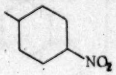
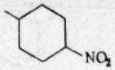
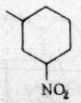
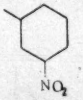
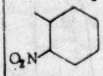
Compound Number	Sulfamides 		Compound Number	Sulfamides 	
	R'	pK_a		R'	pK_a
2		9.60	3		9.55
4		6.60	7		6.65
5		7.35	8		7.20
6		6.70	9		6.65
10		8.45	11		8.35

TABLE 3

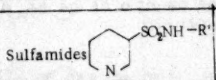
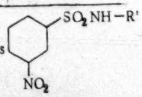
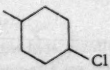
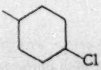
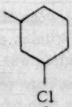
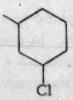
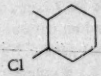
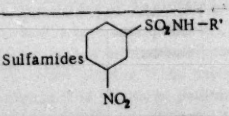
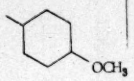
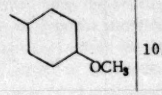
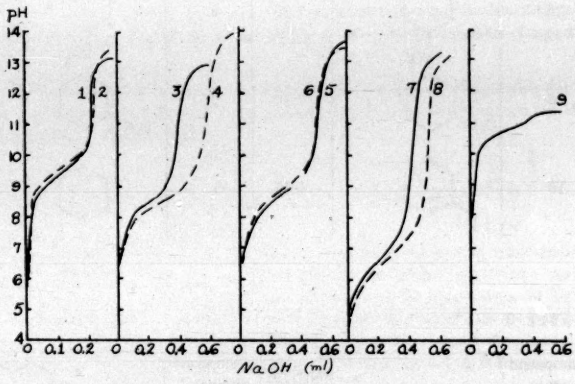
Compound Number	Sulfamides 		Compound Number	Sulfamides 	
	R'	pK_a		R'	pK_a
2		9.60	3		9.55
12		8.70	15		8.60
13		8.45	16		8.35
14		8.20	17		8.10

TABLE 4

Compound Number	Sulfamides R'	pK_a	Compound Number	Sulfamides  R'	pK_a
2		9.60	3		9.55
18		10.05	19		10.00

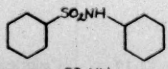
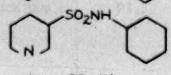
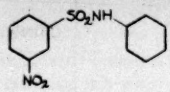
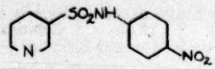
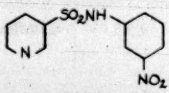
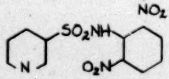
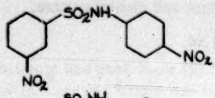
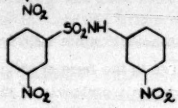
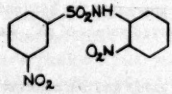
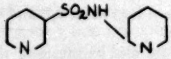
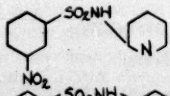
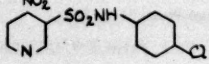
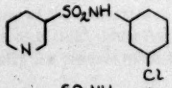
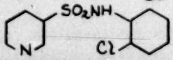
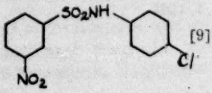


1) β-(N-phenyl)-pyridinesulfamide pH_{et} 11.50, pK_a 9.60; 2) m-nitro-(N-phenyl)-benzenesulfamide pH_{et} 11.25, pK_a 9.55; 3) β-[N-(α-pyridyl)]-pyridine-sulfamide pH_{et} 11.0, pK_a 8.45; 4) m-nitro-[N-(α-pyridyl)]-benzenesulfamide pH_{et} 11.0, pK_a 8.35; 5) β-[N-(p-chlorophenyl)]-pyridine sulfamide pH_{et} 11.20, pK_a 8.70; 6) m-nitro-[N-(p-chlorophenyl)]-benzenesulfamide pH_{et} 11.0, pK_a 8.60; 7) β-[N-(p-nitrophenyl)]-pyridinesulfamide pH_{et} 11.0, pK_a 6.60; 8) m-nitro-[N-(p-nitrophenyl)]-benzenesulfamide pH_{et} 10.25, pK_a 6.65; 9) N-phenylbenzenesulfamide pH_{et} 11.15, pK_a 10.80.

β-Pyridinesulfochloride was prepared by heating β-pyridinesulfonic acid with phosphorus pentachloride and treatment of the product with chloroform (yield 80-85%). Purification was effected by recrystallization from acetone.

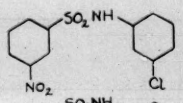
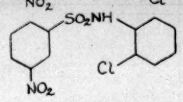
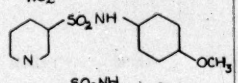
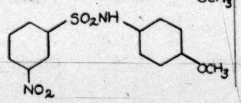
Sulfamides were prepared by the following method, using the preparation of β-(N-phenyl)-pyridinesulfamide as an example (compound 2). In a small round-bottomed flask, provided with an air condenser and a thermometer was put 10 ml dry pyridine and 1.8 g freshly distilled aniline. To the solution was added in small portions 3.6 g β-pyridinesulfochloride; heat was evolved and the mixture acquired a deep orange-red color. The contents of the flask were heated on a water bath for 2 hours at 60-70°. The reaction mass was then poured into water, when an orange oil separated which solidified on trituration and on washing with cold water to a coarse powder. Crystallization from 25-30% aqueous alcohol gave 2.7 g (73.4%) light-orange substance with m.p. 143-144°. Two crystallizations from aqueous alcohol gave 2.1 g colorless substance in the form of flat prisms with constant m.p. of 144-145°.

TABLE 5 *

Compound Number	Formula	Melting point	Analysis for nitrogen		Color
			Calculated	Found	
1	 [6]	112°	–	–	Colorless
2		145	11.96	11.82	Colorless
3		128	–	–	Colorless
4		216	15.10	15.29	Yellow
5		206	15.10	15.00	Cream
6		134	15.10	15.01	Yellow
7		179	13.00	13.15	Yellow
8		152	13.00	13.23	Cream
9		167	13.00	13.25	Yellow
10	 [7]	184	–	–	Colorless
11	 [8]	228-229	–	–	Colorless
12		180	10.44	10.83	Colorless
13		168	10.44	10.63	Colorless
14		127	10.44	10.51	Colorless
15	 [9]	123	–	–	Colorless

* Compounds for which analytical results are not given have been described in the literature and have melting points differing from the literature values by not more than ± 1-2°.

TABLE 5 (Continued)

Compound Number	Formula	Melting point	Analysis for nitrogen		Color
			Calculated	Found	
16		147	11.21	11.17	Colorless
17		149	–	–	Colorless
18		144	10.59	10.30	Colorless
19		134	9.09	8.88	Colorless

Soluble in cold alcohol and acetone; insoluble in water, ether, benzene and dichloroethane.

Found %: N 11.74, 11.82. $C_{11}H_{10}N_2O_2S$. Calculated %: N 11.96.

SUMMARY

1. A number of derivatives of β-pyridinesulfamide and m-nitrobenzene-sulfamide were synthesized.

2. Change in acidic dissociation constants of these compounds is given in the form of pK_a.

3. It was shown that substitution of the benzene ring by a pyridine ring in a molecule of sulfamide of type (I) increases the acidity of the latter, as does also the introduction of a nitro group into the benzene ring (Table 1). For derivatives of β-pyridinesulfamide and m-nitrobenzenesulfamide the observed values of pK_a are identical (Tables 2, 3 and 4).

4. It was shown that substituents such as the electron-accepting nitro group and the chlorine atom increase the acidity of sulfides, whereas the electron-donating methoxyl group reduces it (Tables 2,3 and 4).

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Ural Polytechnic Institute

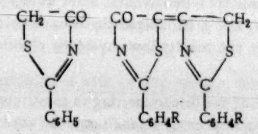
4-KETOTHIAZOLINES (4-HYDROXYTHIAZOLES)

I. SYNTHESIS OF 2-PHENYLTHIAZOLINONE-4 AND ITS DERIVATIVES SUBSTITUTED IN THE BENZENE RING

F. N. Stepanov and Z. Z. Moiseeva

In 1948 Chabrier and co-workers [1] described a series of derivatives of 4-ketothiazoline. Among these we were particularly interested in 2-phenylthiazolinone-4 as an analogy of heterogeneous compounds of the type of pyrazolone and as a possible starting point for synthesis of new dyes.

According to the cited authors 2-phenylthiazolinone-4 (I) is obtained by boiling a solution of thiobenzamide and chloroacetic acid in toluene; it forms yellow crystals with m.p. 250°, insoluble in water, and containing the theoretical amounts of nitrogen and sulfur.



(I) (II) R = H (III) R = p-CF_3.

An earlier attempt had been made [2] to carry out a condensation of this type but had failed. In the opinion of Chabrier and co-workers this failure was due to the use as solvent of alcohol which decomposed the intermediately formed thioiminoethers. This explanation can be fully accepted.

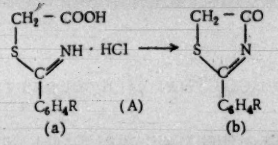
On repeating Chabrier's experiments and making a more detailed examination of the substance with m.p. 250°, it was found that the French investigators had reached erroneous conclusions. The elementary analysis and molecular weight of the substance with m.p. 250° actually correspond to the molecular composition of $C_{18}H_{12}ON_3S_2$ and not to C_9H_7ONS. On the other hand, when the toluene solution (after separation of the substance with m.p. 250°) had stood for 2 days, it deposited a pale-yellow, finely crystalline substance with m.p. 162° (from nitrobenzene). Chabrier and co-workers had overlooked this compound. Its elementary analysis and molecular weight correspond to C_9H_7ONS, and it is 2-phenylthiazolinone-4 (I); it is obtained in a yield of 29% of the theoretical. The compound does not change after boiling for 3 hours in dilute solution (1%) in toluene; on boiling in concentrated (20%) solution, however, it is quantitatively transformed into the substance with m.p. 250°. This transformation also occurs when the substance with m.p. 162° is dissolved in the cold in concentrated sulfuric acid followed by dilution with iced water. The compound has the properties of a weak acid; it dissolves readily in dilute caustic alkali but not in sodium carbonate, and on acidification it comes down unchanged. The substance with m.p. 250° does not dissolve in dilute caustic alkali. Heating of both substances with strong caustic alkali leads to decomposition with formation of benzoic acid, ammonia and hydrogen sulfide. Decomposition of the former compound takes place quantitatively in the course of 3 hours; that of the second compound is not completed even after boiling for many days.

Consideration of the properties of the two compounds leads to the conclusion that 2-phenylthiazolinone-4 (I) is the substance with m.p. 162°, while the substance with m.p. 250°, described by the French workers as 2-phenylthiazolinone-4, is actually the product of its autocondensation — 2-phenyl-5-(2'-phenylthiazolinylidene-4')-thiazolinone-4 (II).

The tendency of 2-phenylthiazolinone-4 to undergo autocondensation is not exceptional; other examples are known of analogous reactions of ketomethylene compounds, for instance acenaphthenone [3].

The structure of the substance with m.p. 162° was conclusively confirmed by its preparation from the hydrochloride of S-(iminobenzyl)-thioglycolic acid — a substance described by Hinkel and Schriner [4] and easily prepared in turn from benzonitrile, thioglycolic acid and dry hydrogen chloride according to scheme (A): (see top of following page).

Boiling for 3 hours of the hydrochloride of S-(iminobenzyl)-thioglycolic acid in ten times the amount of



(IV) R = H; (V) R = p-NO_2; (VI) R = m-NO_2;
(VII) R = p-OCH_3; (VIII) R = p-CF_3.

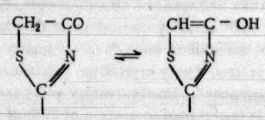
toluene gives a 54% yield of the compound with m.p. 162°, identical with that obtained from thiobenzamide and chloroacetic acid.

2-Phenylthiazolinone-4 can also be prepared from thiobenzamide and ethyl chloroacetate by boiling their mixture in toluene, but it is more conveniently prepared from thiobenzamide and chloroacetic acid. When the reaction is conducted in a solution more dilute than that specified by Chabrier and co-workers, 2-phenylthiazolinone-4 is obtained in a yield of about 60% and without contamination with the product of autocondensation.

Derivatives of 2-phenylthiazolinone-4 substituted in the benzene ring are also readily prepared from the corresponding substituted benzonitriles. Treatment with dry hydrogen chloride of a solution of 4-nitrobenzonitrile and thioglycolic acid in dioxan gives a 70% yield of the hydrochloride of S-(imino-4-nitrobenzyl)-thioglycolic acid (Va). Similarly the respective S-(iminobenzyl)-thioglycolic acids were prepared from 3-nitrobenzonitrile (80%) (VIa), 4-methoxybenzonitrile (23%) (VIIa) and 4-trifluoromethylbenzonitrile (78%) (VIIIa). It is interesting to note that the hydrochloride (VIIIa) is not stable and readily loses hydrogen chloride on heating and on treatment with water.

Of great importance for the closure of the thiazoline ring in substituted S-(iminobenzyl)-thioglycolic acids are the reaction conditions. Thus, 2-(4'-nitrophenyl)-thiazolinone-4 (Vb) is obtained in 52%) yield under relatively mild conditions [boiling of (Va) in 10% benzene solution], whereas the 3'-nitroisomer (VIb) is obtained in 60% yield in 2.5% toluene solution. Similarly to the 3'-nitro isomer is obtained the 4'-methoxy derivative (VIIb) in 74% yield.

Unlike other derivatives, 2-(4'-trifluromethylphenyl)-thiazolinone-4 (VIIIb) has such a great tendency to autocondense that in its place we obtain exclusively 2-(4'-trifluoromethylphenyl)-5-(4"-trifluromethylphenylthiazolinylidene-4')-thiazolinone-4 (III) when the ring-closure reaction is carried out in toluene; in benzene solution the closure does not take place at all and unchanged (VIIIa) is isolated.



The thiazolinone-4 system is tautomeric with the 4-hydroxythiazole system; however, the chemical properties of 2-phenylthiazolinone-4 (reactions with aldehydes, formation of polymethine and azomethine dyes) point to the predominance, if not to the exclusive existence, of the carbonyl form. Nevertheless 2-phenylthiazolinone-4 is easily acylated. Treatment with benzoylchloride in benzene solution in presence of pyridine at 60-70° results in formation of the monobenzoyl derivative. On boiling (I) with acetic anhydride, acetylation is accompanied by autocondensation and the monoacetyl derivative (II) is formed. The same substance is also formed on boiling (II) with acetic anhydride. The question as to whether these compounds have the structure of O-acyl or C-acyl derivatives still remains unsettled.

2-Phenylthiazolinone-4 and its derivatives substituted in the benzene ring possess weakly acid properties. Qualitative comparison shows that the most acidic is the 4-nitro derivative (Vb), which is soluble not only in caustic alkalies but also in sodium carbonate solution.

EXPERIMENTAL

Condensation of thiobenzamide with chloroacetic acid. 1) A mixture of 3 g chloroacetic acid, 3 g thiobenzamide and 30 ml toluene is boiled 3 hours. The hot solution is filtered from the separated ammonium chloride. The yellow precipitate which comes down on cooling is separated and washed with toluene and ether. Weight of product (II) 0.9 g (12% calculated on the benzamide). After three crystallizations from nitrobenzene, yellow, microscopic needles with m.p. 249-250°.*

* All melting points are uncorrected.

Found %: C 64.23, 64.01; H 3.81, 3.78; S 19.07, 18.94; N 8.33, 8.14. M 357 (in camphor). $C_{18}H_{12}ON_2S_2$. Calculated %: C 64.22; H 3.62; S 19.02; N 8.33. M 336.

After 2-days' standing, the main toluene filtrate deposited 1.2 g yellowish crystals of (I) (29% calculated on the thiobenzamide). After recrystallization from nitrobenzene, m.p. 162°.

Found %: C 60.94, 60.96; H 4.17, 4.09; S 17.74, 17.75; N 7.73, 7.92. M 181 (in naphthalene). C_9H_7ONS. Calculated %: C 60.98, H 3.99; S 18.08; N 7.91. M 177.

2) A mixture of 3.4 g chloroacetic acid, * 5 g thiobenzamide and 100 ml toluene is boiled 3 hours. Under these conditions product (II) is not formed at all, and after 2-days' standing at room temperature, product (I) comes down from the filtered (hot) reaction mixture in the amount of 3.6 g (55.7%). The substance melts at 162° (from nitrobenzene). A mixed sample with (I) prepared under the above-described conditions does not show a melting point depression.

Condensation of 2-phenylthiazolinone-4. A mixture of 1 g (I) and 5 ml toluene is boiled 3 hours. The substance goes into solution 2 hours after the start of boiling. On cooling, the crystalline precipitate is collected and washed with toluene and ether. Yield 0.8 g (84%) of (II).

The substance does not change after 3-hours' boiling of 0.2 g (I) in 20 ml toluene.

0.5 g (I) is dissolved in 5 ml concentrated sulfuric acid in the cold, and the solution is poured into 20 ml iced water. The precipitate of (II) is separated and washed with water. The dried substance weighs 0.4 g (84%); m.p. 249-250° after recrystallization from nitrobenzene, and no depression of melting point in admixture with the previous preparation.

Decomposition of 2-phenylthiazolinone-4 with caustic alkali. A weighed amount is boiled with excess concentrated alkali in a Kjeldahl apparatus, and the evolved ammonia is absorbed in 0.1 N hydrochloric acid (3 hours). The solution in the distillation flask is then acidified with sulfuric acid and boiled until hydrogen sulfide ceases to come off (about 3 hours); the latter is taken up in 0.1 N caustic alkali solution. Ammonia is determined in the distillate by back titration with caustic alkali, and the hydrogen sulfide is determined iodometrically. Benzoic acid is determined in a separate, larger, sample, after separating it from the residue after distillation of the hydrogen sulfide; m.p. 121-122°.

Found %: N 7.72, 7.59; S 17.87, 17.72. C_9H_7ONS. Calculated %: N 7.91; S 18.08.

Condensation of benzonitrile and its derivatives with thioglycolic acid. 1) Into 50 ml anhydrous ether, saturated at 0° with hydrogen chloride, are introduced 2 g benzonitrile and 4 g thioglycolic acid. The mixture is left at 0° for 3 days in a closed flask [4]. Compound (IVa) comes down as colorless, lustrous needles and is separated and washed with ether. Yield 1.8 g, decomposition temp. 125° (124-125° [4]).

0.8 g (IVa) and 8 ml toluene are boiled 3 hours. The filtered and cooled solution is stood 2 days at room temperature. The precipitated substance is separated and washed in succession with toluene, alcohol and ether. Yield 0.33 g (54%). M.p. 162° after recrystallization from nitrobenzene; no depression in admixture with the compound prepared from thiobenzamide and chloracetic acid.

Found %: N 7.72. C_9H_7ONS. Calculated %: N 7.91.

2) 5 g p-nitrobenzonitrile is dissolved in 50 ml dioxan. Into the solution is introduced 10 g thiolbycolic acid, and the mixture is saturated at 0° with dry hydrogen chloride until the weight increase is 25 g. The solution is stood 3 days at room temperature. The separated product (Va) is collected and washed with dioxan and ether. Yield 6.5 g (70%). Light-yellow needles, m.p. 140°.

Found %: Cl 12.79. $C_9H_9O_4N_2SCl$. Calculated %: Cl 12.83.

A mixture of 2 g (Va) and 20 ml benzene is boiled 3 hours. The substance (Vb) coming down on cooling is separated and washed with benzene. Yield 1.67 g (52%). Yellow prismatic needles from alcohol, m.p. 177-178°. Insoluble in water, soluble in sodium carbonate solution (comes down on acidification).

Found %: C 48.97, 48.75; H 2.77, 2.76; S 14.26, 14.36; N 12.94. $C_9H_6O_3N_2S$. Calculated %: C 48.64; H 2.73; S 14.42; N 12.60

3) 3 g m-nitrobenzonitrile is dissolved in 25 ml dioxan. 8 g thioglycolic acid is added, and the mixture saturated at 0° with dry hydrogen chloride to a weight increase of 10 g. The solution is left 3 days at room temperature. The precipitate (VIa) is separated and washed with dioxan and ether. Yield 4.5 g (80%). Colorless needles, m.p. 154° (with decomp.).

Found %: Cl 12.74. $C_9H_9O_4N_2SCl$. Calculated %: Cl 12.83.

* The acid can be replaced by 5 g of its ethyl ester, but the yield is then approximately halved.

A mixture of 3.3 g (VIa), 135 ml toluene is boiled 3 hours and filtered hot. The compound (VIb) which comes down after 2 days is collected and washed with ether. Yield 1.6 g (60%). Yellow needles from glacial acetic acid, m.p. 179-180°.

Found %: C 48.88, 48.68; H 3.10, 2.90; S 14.60, 14.90; N 12.61. $C_9H_6O_3N_2S$. Calculated %: C 48.64; H 2.73; S 14.42; N 12.60.

4) 6 g p-methoxybenzonitrile is dissolved in 40 ml dioxan, 12 g thioglycolic acid is added, and the mixture saturated with hydrogen chloride at 0° to a weight increase of 22 g. The solution is left at room temperature 3 days. The precipitate of (VIIa) is separated and washed with dioxan and ether. Yield 2.8 g (23%). Lustrous, colorless needles, m.p. 162-163°.

Found %: Cl 13.40. $C_{10}H_{12}O_3NSCl$. Calculated %: Cl 13.54.

A mixture of 0.6 g (VIIa) and 6 ml toluene is boiled 3 hours. The filtered solution is cooled. The precipitate (VIIb) is separated and washed with ether. Yield 0.35 g (73%). Pale-yellow needles from alcohol, m.p. 143°.

Found %: C 58.15, 58.30; H 4.57, 4.52; S 15.67, 15.50; N 6.60. $C_{10}H_9O_2NS$. Calculated %: C 57.95; H 4.38; S 15.46; N 6.76.

5) 2 g p-trifluromethylbenzonitrile and 4 g thioglycolic acid are introduced into 15 ml dioxan, and saturated at 0° with hydrogen chloride; the mixture is left at room temperature 24 hours. The mass is diluted with 60 ml water, the precipitate [(VIIIa – the free imino acid] is separated, washed with water until neutral and dried. Yield 2.6 g (84%). Colorless, microscopic needles, m.p. 175-176°. Found %: N 5.43, 5.49. $C_{10}H_8O_2NSF_3$. Calculated % N 5.32.

1 g (VIIIa) and 20 ml toluene were boiled for 3 hours. On cooling the filtrate yielded substance (III) of slightly colored prisms. Yield 0.7 g (78%), m.p. 181-182°.

Found %: F 14.25, 24.55. M 480 (in naphthalene). $C_{20}H_{10}ON_2S_2F_6$. Calculated %: F 24.13, M 472.

Acylation of 2-phenylthiazolinone-4. a) 1 g (I) is boiled with 10 ml acetic anhydride for 10 minutes. The finely crystalline acetyl derivative (II) comes down on cooling. Yield 1.2 g (56%).. After crystallization from acetic anhydride, m.p. 164°.

Found %: C 63.30; H 3.70; S 17.23; N 7.38. $C_{20}H_{14}O_2N_2S_2$. Calculated %: C 63.46; H 3.74; S 16.94; N 7.41.

The same substance is obtained on acetylating substance (II) under the same conditions.

b) To a solution of 0.5 g (I) in 10 ml benzene and 5 ml pyridine is added 0.5 g benzoyl chloride, and the mixture is heated 30 minutes at 60-70°. The mass is poured on to 10 ml iced water and the benzene layer is separated and washed twice with water. Distillation of the benzene leaves the benzoyl derivative in the form of crystals. Two crystallizations from benzene give 0.3 g substance with m.p. 220-221°.

Found %: C 68.06; H 3.97; N 4.95; S 11.60. $C_{15}H_{11}O_2NS$. Calculated %: C 68.32; H 3.91; N 4.98; S 11.66.

SUMMARY

1. The substance described by Chabrier and co-workers as 2-phenylthiazolinone-4, m.p. 250°, is actually the product of its autocondensation – 2 phenyl-5-(2'-phenylthiazolinylidene-4')-thiazolinone-4 (II).

2. 2-Phenylthiazolinone-4 (I) is obtained in good yield by boiling thiobenzamide and chloroacetic acid in dilute toluene solution and has m.p. 162°.

3. 2-Phenylthiazolinone-4 and its derivatives substituted in the benzene ring (with p-NO_2, m-NO_2, p-CH_3O) can be obtained by closure of the thiazoline ring in S-(iminobenzyl)-thioglycolic acid and its derivatives by heating their benzene or toluene solutions.

4. 2-Phenylthiazolinone-4 is a very weak acid and manifests phenolic properties in its ability to be acylated.

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K.E. Voroshilov Institute of Scientific Research for Intermediates and Dyes

THE PROBLEM OF THE HYDROGENATION OF THE FURAN RING

N.I. Shuikin, V.A. Tulupov and I.F. Belsky

The hydrogenation of the furan ring has been studied by many investigators. In a survey [1] covering the material on hydrogenation of furan compounds up to 1950, attention is drawn to the possibility of applying this reaction to the synthesis of diverse organic compounds. Many studies have been carried out to establish the conditions for maximum conversion of furan and 2-methylfuran into their hydrogenated derivatives from which are subsequently obtained butadiene and piperylene (1,3-pentadiene). In papers by N.D. Zelinsky and N.I. Shuikin [2] and by N.I. Shuikin and coworkers [3,4] it was shown that in presence of finely dispersed osmium on asbestos, of palladium and nickel on nickel-aluminum alloy at various temperatures, furan and a number of its homologs are nearly quantitatively transformed into the corresponding tetrahydro derivatives.

In a number of researches [5,6,7], however, it was established that the furan ring is ruptured at the C—O bond during hydrogenation. Hydrogenation of furan was accompanied, for example, by formation of n-butyl alcohol, while 2-methylfuran also gave pentanol-1, pentanol-2 and pentanone-2.

In the case of furfuryl alcohol, rupture of the ring at the C—O bond led to formation of dihydric alcohols [8-10].

We embarked on a more detailed investigation of the products formed during hydrogenation of furan and 2-methylfuran in presence of nickel catalyst with the additional objective of determining the place of preferential rupture of the furan ring. Hydrogenation was conducted in a flow system over nickel prepared by the method described by one of us [3]. Furan was hydrogenated at 200°, 2-methylfuran at 125 and 200° at a space velocity of 0.06 $hour^{-1}$ in excess of hydrogen.

1 kg 2-methylfuran and 200 g furan were taken for hydrogenation; these amounts permitted the detection of any products of the reaction formed in small quantities.

The reaction products were subjected to fractional distillation in columns with efficiencies of 30 and 70 theoretical plates. The fractionation curves revealed the presence of narrow cuts which represented pure substances, azeotropes or mixtures of substances with close boiling points.

After determination of the main physical constants, the prepared alcohols were identified by conversion to their 3,5-dinitrobenzoates, and the ketones through the corresponding semicarbazones. The gases were collected in a liquid nitrogen-cooled trap and analyzed in the VTI (All-Union Heat Engineering Institute) apparatus.

Results of investigation of the catalyzates are presented in Tables 1-3.

TABLE 1

Products of catalytic hydrogenation of furan at 200°

Products of hydrogenation	Yield (in %)	Boiling point (corrected)	d_4^{20}	n_D^{20}	Melting point of esters of 3,5-dinitrobenzoic acid
Furan	15	31-32°	0.9374	1.4212	—
Methanol	3	64-65	—	—	108-109°
Tetrahydrofuran	37	65-66	0.8879	1.4070	—
Propanol-1	5	97-98	0.8042	1.3860	74-75
Butanol-1	10	116-117	0.8104	1.3996	61-62
Water + gases	30	—	—	—	—

Compounds whose physical properties are not listed in the tables were isolated from azeotropes or from mixtures of substances with close boiling ponts in the form of their derivatives (esters, semicarbazones).

The data of Table 1 show that hydrogenation of furan is accompanied by cleavage of the ring at the C—O and C—C bonds with formation of n-butyl, n-propyl and methyl alcohols. More far-reaching breakdown of the furan ring also occurs to a considerable extent and leads to formation of water and gases.

The principal products of hydrogenation of 2-methylfuran at 125° (Table 2) are tetrahydro-2-methylfuran (85%) and alcohols; a little pentanone-2 is also formed. Products of rupture of the furan ring make up about 15%. At 200° (Table 3) ketones predominate in the products of hydrogenation of 2-methylfuran; alcohols are present in insignificant amount; the total content of products of furan ring cleavage (up to 80%) increases sharply. In contrast to furan, the

TABLE 2 *

Products of catalytic hydrogenation of 2-methylfuran at 125°

Products of hydrogenation	Yield (in %)	Boiling point (corrected)	d_4^{20}	n_D^{20}	Melting point of esters of 3,5-dinitrobenzoic acid
Methanol	2	–	–	–	109-110°
Ethanol	5	–	–	–	93-94
Butanol-2	30	98-99.5°	0.8073	1.3932	75-76
Pentanone-2	2	101-102	–	–	–**
2-Methylbutanol-2	2	101-102	–	–	81.5-82.5
Pentanol-2	40	118-119	0.8096	1.4060	61-62
2-Methylbutanol-1	4	–	–	–	70-71
Pentanol-1	6	137-138	0.8178	1.4125	45-46
Residue with b.p. > 138°	8	–	–	1.4312	–

TABLE 3 *

Products of catalytic hydrogenation of 2-methylfuran at 200°

Products of hydrogenation	Yield (in %)	Boiling point	d_4^{20}	n_D^{20}	Melting point of esters of 3,5-dinitrobenzoic acid	Melting point of semicarbazones
Methanol	2	–	–	–	109-110°	–
Ethanol	10	–	–	–	93-94	–
Butanone-2	25	–	–	–	–	147-148°
Butanol-2	5	98-99.5°	0.8076	1.3937	75-76	–
Pentanone-2	40	101-102	0.8109	1.3906	–	110-111
Pentanol-2	5	118-119	0.8087	1.4052	61-62	–
2-Methylbutanol-2	4	–	–	–	81.5-82.5	–
Pentanol-1	5	137-139	0.8191	1.4121	45-46	–
Residue with b.p. > 139°	4	–	–	1.4336	–	–

butanol at the C–C bond according to the scheme:

$$CH_3 \vdots CH_2CH_2CHOHCH_3 \xrightarrow{H_2} CH_4 + CH_3CH_2CHOHCH_3$$

or 2) by simultaneous rupture of the C–O and C–C bonds in the reaction complex formed during hydrogenation of the furan ring at the catalyst surface.

Pentanol-2 was passed over the same nickel catalyst under hydrogenation conditions at 125°. Under these conditions it is not converted into alcohols with a smaller number of carbon atoms but only undergoes minor dehydrogenation to methylpropyl ketone. Nor was isomerization of pentanol-2 to iso alcohols observed. We are therefore left with the possibility of simultaneous rupture of the C–O and C–C bonds during hydrogenation of the furan ring.

We shall assume that alcohols with a smaller number of carbon atoms are formed as a result of pairwise ("coupled") ruptures of the C–O and C–C bonds; this process can yield the following alcohols:

1) From furan (A): methanol (rupture of the 4-5 and 1-2 bonds or of 2-3 and 1-5), ethanol (cleavage of the 3-4 and 1-2 or 3-4 and 1-5 bonds), propanol-1 (cleavage of the 1-5 and 4-5 or 1-2 and 2-3 bonds).

2) From 2-methylfuran (B): methanol (cleavage of the 1-2 and 4-5 bonds), ethanol (cleavage of the 2-3 and 1-5 or 3-4 and 1-2 bonds), propanol-1 (cleavage of the 1-2 and 2-3 bonds), propanol-2 (cleavage of the 3-4 and 1-5 bonds),

furan ring is only broken down to water and gases to a very slight extent in the hydrogenation of 2-methylfuran. The gases consist mainly of methane (90%); Paraffinic hydrocarbons with a larger number of carbon atoms are formed in minute amount.

A new fact which emerges from our work is the formation of alcohols and ketones with a number of carbon atoms smaller than in furan or tetrahydrofuran, and also of amyl alcohols with an iso structure. Formation of alcohols with a smaller number of carbon atoms can occur by two routes:

1) By a secondary process of hydrocracking of the amyl alcohols or of the

* In Tables 2 and 3 the total content of products of cleavage of the furan ring is assumed to be 100%.

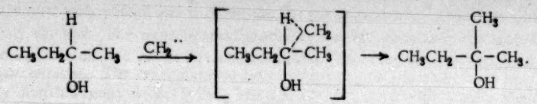
** M.p. of semicarbazone 110-111°.

butanol-2 (cleavage of the 1-5 and 4-5 bonds).

(A)

(B)

Coupled cleavage of the 1-5 and 4-5 bonds can lead to formation, apart from an alcohol, of the $CH_2^{\cdot\cdot}$ radical which can be hydrogenated to methane or methylated to other molecules. Since no isomerization of pentanol-2 to iso alcohols was observed under the hydrogenation conditions, it may be suggested that 2-methylbutanol-2 is formed as a result of methylation of butanol-2 by the methylene radical:



The mechanism of formation of 2-methylbutanol-1 is still obscure.

The absence of ethanol from the products of hydrogenation of furan and of isopropanol from those of 2-methylfuran can be explained on the assumption that the rupture of the bond between carbon atoms 3 and 4, necessary for formation of these alcohols, is either hindered or does not take place at all. In the complex absorption the C=C bonds are evidently weakened in very high degree due to the intensive action of hydrogen atoms upon them. This factor leads us to anticipate a differing behavior of the furan and tetrahydrofuran rings under identical hydrogenation conditions. This theory was tested by passing tetrahydro-2methylfuran over nickel deposited on nickel–aluminum alloy at 200° under conditions identical with those for the hydrogenation of 2-methylfuran. The greater part of the tetrahydro-2-methylfuran remained unchanged. Products of cleavage of the tetrahydrofuran ring amounted to not more than 10%, whereas in the hydrogenation of 2-methylfuran they reached 80%. The partial cleavage of the tetrahydrofuran ring took place mainly at the C–O bond [1,5], which led at 200° to formation of pentanone-2. At the same time butanol-2 and ethanol were also formed in amounts very much smaller than in the hydrogenation of 2-methylfuran.

Thus the hydrogenated furan ring manifests a very much lower susceptibility to cleavage than the furan ring under hydrogenation conditions: not only is cleavage of the C–C bond hindered, but the C–O bond proves to be more stable.

Tables 2 and 2 show that hydrogenation of 2-methylfuran is accompanied by very facile rupture of the 1-5 bond and by coupled rupture of the 1-5 and 4-5 bonds, leading to formation of, respectively, pentanol-2 and butanol-2.

The considerable stability of the 1-2 and 2-3 bonds under hydrogenation conditions is evidently due to the steric influence of the methyl group. The difficulty of coupled cleavage of the 1-2 and 2-3 bonds accounts for the absence of n-propanol from the products of hydrogenation of 2-methylfuran.

SUMMARY

1. Hydrogenation of the furan ring is accompanied, apart from cleavages of the C–O bonds, by paired (coupled) cleavages of the C–O and C–C bonds. Cleavages of the C–C bond alone are not observed.

2. The methyl group in 2-methylfuran exerts a screening action upon its neighboring C–O and C–C bonds, lowering their susceptibility to cleavage under hydrogenation conditions.

3. The tetrahydrofuran ring is very much more resistant to hydrogenation than the furan ring under identical hydrogenation conditions.

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Moscow State University

THE REACTION OF ETHANOLAMINE WITH PHENOL AND o- AND p-CHLOROPHENOLS

D.E. Dionisyev and M.G. Kosareva

We have applied the methods of fusibility, viscosity, density and electrical conductivity to a study of the binary systems formed by ethanolamine with phenol and p-chlorophenol; the system ethanolamine-o-chlorophenol has been studied only by the fusibility method. The experimental procedure was the same as in the preceding studies [1]; measurements in the liquid phase were carried out at three temperatures. The viscosity was expressed in centipoises, the concentrations in molar percentages. The ethanolamine used in the research was dried for a long period over solid KOH and then fractionally distilled many times; it then had b.p. 171°, m.p. 10°, d_4^{20} 1.020. Phenol, and o- and p-chlorophenols were thoroughly purified by numerous fractional distillations and had the following constants:

Phenol – m.p. 41.5°, b.p. 181°, d_4^{50} 1.051; p-chlorophenol – b.p. 217°, m.p. 37°, d_4^{40} 1.251; o-chlorophenol – b.p. 175.5°, m.p. 7°.

System ethanolamine-phenol. The fusibility curve (Fig. 1, a) contains two eutectic points and one maximum. The first eutectic point with m.p. 23° corresponds to 20 mole-% ethanolamine, the second eutectic point with m.p. −20° corresponds to 33.3 mole-%. The fusibility curve indicates that ethanolamine and phenol form a compound with the composition $HOC_2H_4NH_2 \cdot 2C_6H_5OH$ with a ratio of components of 1:2.

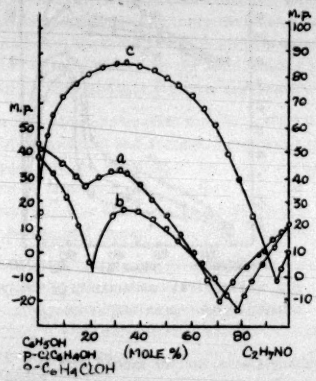

Fig. 1. Fusibility of the systems: phenol–ethanolamine (a), p-chlorophenol–ethanolamine (b), o-chlorophenol–ethanolamine (c).

Left-hand scale – curves (a) and (b); right-hand scale – curve (c).

The density d and the viscosity η of this system were studied at 35, 45 and 55°. Results of measurements of density and viscosity are represented in Fig. 2. Only the 55° isotherm was plotted for the whole of the concentration range.

The viscosity isotherms pass through a maximum in the region of 50 mole-% of components. The viscosity of mixtures decreases appreciably with rising temperature, but the maximum is only shifted to a very slight extent in the direction of the more viscous component – ethanolamine. The temperature coefficient of viscosity γ has a maximum exactly corresponding to 50 mole-%, which points to a compound of 1:1 composition.

Consequently, interaction between the components in the liquid phase gives a compound with equimolecular composition which was not revealed by the fusibility method. The 1:2 compound found by the fusibility method was not reflected on the viscosity isotherms.

The density isotherms are slightly convex to the axis of composition, indicating a slight contraction in the system.

The isotherms of electrical conductivity κ (Fig. 3) are curves which are convex to the axis of composition and have a very diffuse maximum which corresponds to approximately 70 mole-% ethanolamine. Correction of the electrical conductivity for viscosity $\kappa\eta$ results in curves with a well-defined maximum which corresponds to 50 mole-% ethanolamine.

In the opinion of M.I. Usanovich [2] the persistence of the maximum on the "corrected" electrical conductivity curve testifies to the occurence of an acid-base interaction. The curve of the temperature coefficient of electrical conductivity α has the same shape as the electrical conductivity isotherms.

Consequently, inspection of the above curves permits us to conclude that this system in the liquid phase contains an equimolar compound which is reflected in the isotherms of viscosity, temperature coefficient of viscosity and "corrected" electrical conductivity.

System ethanolamine-p-chlorophenol. The fusibility curve (Fig. 1, b) has two eutectic points and one maximum.

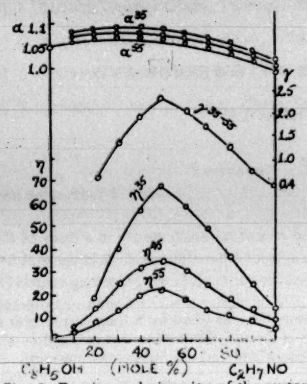

Fig. 2. Density and viscosity of the system phenol – ethanolamine.

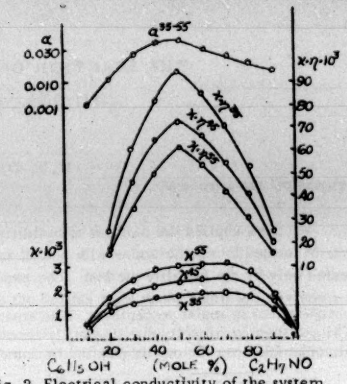

Fig. 3. Electrical conductivity of the system phenol – ethanolamine.

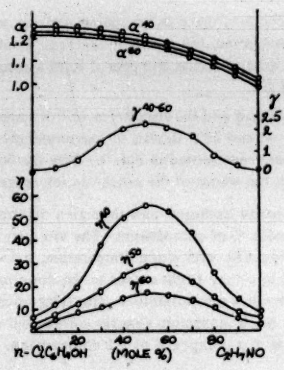

Fig. 4. Density and viscosity of the system ethanolamine – p-chlorophenol.

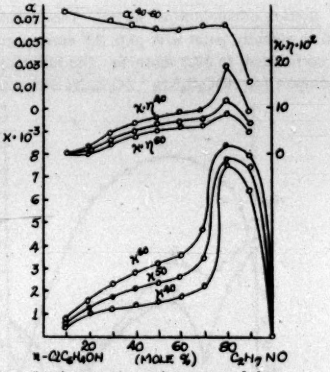

Fig. 5. Electrical conductivity of the system ethanolamine – p-chlorophenol.

The first eutectic point with m.p. −7° corresponds to 21 mole-% ethanolamine, and the second with m.p. −22° to 80 mole-% ethanolamine. The maximum with m.p. 17° corresponds to 33.3 mole-% ethanolamine and has the composition $HOC_2H_4NH_2 \cdot 2p\text{-}C_6H_4ClOH$ with a ratio of components of 1:2; this compound does not crystallize well. During formation the compound releases heat.

Results of measurement of viscosity and density at 40, 50 and 60° are plotted in Fig. 4 and those of electrical conductivity in Fig. 5. The form of the density isotherms is similar to that of the density isotherms in the system ethanolamine – phenol. The viscosity isotherms rise steeply from the value of the viscosity of ethanolamine itself, pass through a maximum at 50 mole-% ethanolamine, and also descend steeply to the value of the viscosity of p-chlorophenol itself.

The curve of the temperature coefficient of viscosity, which follows the course of the viscosity isotherm, also has a maximum in the region of 50 mole-% ethanolamine.

Consequently, just as in the preceding system, the liquid phase contains a compound with equimolar composition which is not reflected in the fusibility curve. The compound with the 1:2 composition (2 molecules of p-chlorophenol), detected by the fusibility method, is not reflected on the viscosity isotherms.

The electrical conductivity isotherms (Fig. 5) have maxima corresponding to 80 mole-% ethanolamine. When the electrical conductivity is corrected for viscosity, the maxima persist for the same compositions. The appearance of a maximum on the electrical conductivity isotherms and its persistence after correction of the electrical conductivity

for viscosity point to a reaction in the system manifested in the formation of an electrically conductive compound.

In the present case, however, the position of the maximum on the electrical conductivity isotherms "uncorrected" and "corrected" for viscosity, and even more so the position on the curve of the temperature coefficient of the conductivity, does not give adequate indication of the composition of the compound. It is evident that such a large shift of the maximum in the direction of ethanolamine is due to the circumstance that concentrations of about 50 mole-% of components correspond to a high viscosity and a lower electrical conductivity.

Hence on the basis of the curves obtained, the conclusion can be reached that in this system in the liquid phase a compound with 1:1 composition exists and is reflected on the viscosity isotherms and on the curve of the temperature coefficient of viscosity, while a compound with 1:2 composition (2 molecules p-chlorophenol) crystallizes from the melts.

System ethanolamine -- o-chlorophenol. It follows from the fusibility diagram of this system (Fig. 1, c) that the components interact with formation of a 1:2 compound (2 molecules of o-chlorophenol). The maximum on the fusibility diagram with m.p. 87.5° corresponds to 33.3% ethanolamine. The first eutectic point approaches very close to the side of o-chlorophenol and corresponds to a fraction of a percent of the ethanolamine content of the mixture. A similar case was observed by M. S. Elgort in a study of systems formed by ethylene diamine with palmitic and stearic acids [3]. The second eutectic point with m.p. −3° corresponds to 94 mole-% ethanolamine. Heat is released during formation of the compound.

Evaluation of results. Investigations of the system formed by phenol with ethylene diamine [4], hydrazine [5] and urea [6] showed that phenol forms a 1:2 compound (2 molecules of phenol) with diamines. N. Perrakis [7] established the absence of interaction of ethyl alcohol with phenol. From these facts it follows that in ethanolamine, which is a derivative of ethyl alcohol, only the amino group takes part in the formation of the compound with phenol. Our experimental data showed that in the system ethanolamine-phenol, chemical interaction was detected both in the liquid and in the solid phase. In the solid phase a 1:2 compound was detected, however, while in the liquid phase the presence of a compound of equimolar composition was established.

The following explanation may be given: It is known that monobasic organic acids, alcohols and phenols are considerably associated and at room temperature they consist of dimers. Ethanolamine functions as a donor of one electron pair, and the hydrogen of the dimer accepts this pair with formation of a 1:2 compound. Association is accounted for by formation of a hydrogen bond; the latter requires a small activation energy for its formation and also for its cleavage. The same applies to this system in the liquid phase: at a higher temperature the hydrogen bond is evidently broken and an equimolecular compound is formed in the system.

Introduction of chlorine into the phenol molecule ought to increase the reactivity of the hydroxyl group. And indeed an investigation of the reaction of o- and p-chlorophenol with ethanolamine revealed the presence in the solid phase of a compound of the same composition as with phenol, but the melting point of the compound with o-chlorophenol (87.5°) is very much higher than the melting point of the compound with phenol (30°) and p-chlorophenol (17°). These observations lead to the conclusion that o-chlorophenol has a greater affinity for ethanolamine than phenol and p-chlorophenol.

SUMMARY

1. Binary systems formed by ethanolamine with phenol and p-chlorophenol were studied by the methods of determination of fusibility, density, viscosity and electrical conductivity; the system with o-chlorophenol was studied by the fusibility method.

Compounds of the following composition exist in the systems ethanolamine − phenol, ethanolamine − o- and p-phenol: in the solid phase:

$$HOC_2H_4NH_2 \cdot 2C_6H_5OH,\ HOC_2H_4NH_2 \cdot 2o\text{-}C_6H_4ClOH \text{ and } HOC_2H_4NH_2 \cdot 2p\text{-}C_6H_4ClOH.$$

3. Compounds of equimolecular composition were detected in the systems ethanolamine -- phenol and ethanolamine − p-chlorophenol.

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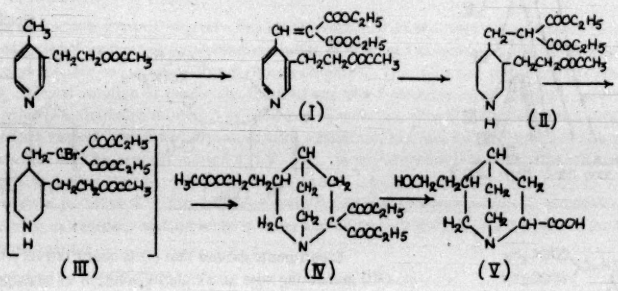
Rostov State University

SYNTHESIS OF 5-(β-HYDROXYETHYL)-QUINUCLIDINE-CARBOXYLIC ACID-2

M.V. Rubtsov and L.N. Yakhontov

Relatively few studies have been made of the quinuclidine ring, a component of quinine alkaloids. 2,5-Disubstituted quinuclidines, with the exception of the quinine alkaloids and their transformation products, have not been described.

Application of a simple method of synthesis of quinuclidinecarboxylic acid-2, previously developed by one of us [1] and M.I. Dorokhova, enabled us to obtain the previously undescribed 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2. The synthesis was realized by the following scheme:



3-(β-Acetoxyethyl)-4-methylpyridine [2], prepared from trichlorocollidine, was subjected to condensation with dihydroxymalonic ester.

Employment of dihydroxymalonic ester *, a crystalline substance, avoids contamination with the impurities which accompany the mesoxalic ester and which considerably lower the yield of 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine.

Condensation of 3-(β-acetoxyethyl)-4-methylpyridine with dihydroxymalonic ester gives a mixture of substances from which two compounds with m.p. 111-112° (I) and with m.p. 147-148° (VI) are isolated in the form of their hydrochlorides.

The compound with m.p. 111-112° contains a double bond (reaction with potassium permanganate) and an acetoxy group (ethyl acetate is formed on boiling with alcoholic hydrogen chloride). On the basis of these properties, of the method of preparation, and of the elementary analysis, the compound with m.p. 111-112° must be assigned the structure of 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine (I) hydrochloride. The elementary analysis of the compound with m.p. 147-148° indicates that it is $C_{15}H_{19}NO_5 \cdot HCl$; it does not give a reaction for the double bond with potassium permanganate and contains no hydroxy group (it is not acetylated by acetyl chloride at room temperature or with acetic anhydride at the boil). These properties indicate that compound (VI) has a bicyclic structure. This surmise is confirmed by comparing the graphs of extinction coefficient versus wavelength for the ultraviolet spectra of the compounds (I) and (VI) that we prepared and also of the bicyclic pyridinodihydropyrancarboxylic acids and their esters described by M.V. Rubtsov [2] (see diagram).

Saponification and decarboxylation of compound (VI) led to the formation of an acid with m.p. 192-194°, identical with "acid B" obtained by M.V. Rubtsov during saponification of 3-(β-acetoxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine. M.V. Rubtsov assigns one of two formulas to "acid B": 6-methyl-4,5-(3',4'-pyridino)-dihydropyran-2-carboxylic acid (VII) or 3,4-(3',4',-pyridino)-dihydropyran-2-acetic acid (VIII):

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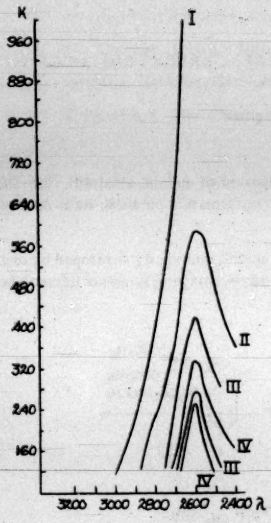
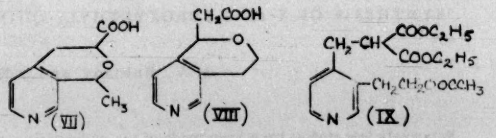
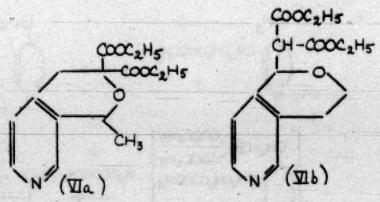
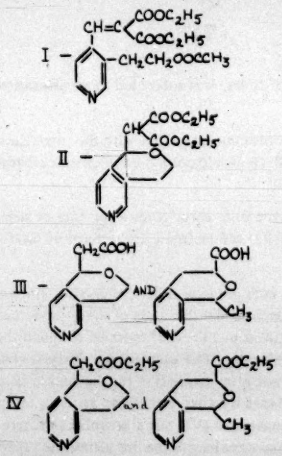
* Dihydroxymalonic ester was prepared by oxidation of ethyl malonate with selenium dioxide [3] followed by addition of the calculated amount of water to the twice-distilled mesoxalic ester.



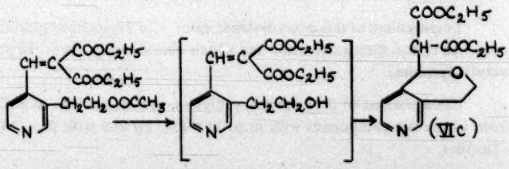


On the basis of the foregoing considerations, one of two formulas may correspond to substance (VI):





Experiments showed that (I) is quantitatively transformed into (VI) on heating with an alcoholic solution of hydrogen chloride, and ethylacetate is formed at the same time. The process apparently takes place in two steps in the following order:



This scheme of the process, in our opinion the most probable, permits us to assume for compound (VI) the structure of 2-dicarbethoxymethyl-3,4-(3',4'-pyridino)-dihydropyran (VIb).

The hydrochloride of 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine (I) was hydrogenated in presence of platinum catalyst in a medium of anhydrous alcohol. Hydrogenation takes place in two steps. The first step – reduction of the vinyl group – goes quickly and and is complete in 2-3 hours, whereas hydrogenation of the pyridine ring goes much more slowly (15-20 days). This permits isolation and characterization of the intermediate compound – 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyethyl)-pyridine (IX).

The end product of hydrogenation – 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine (II) was converted with bromine into 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxybromethyl)-piperidine (III). The prepared bromo derivative (III) is readily cyclized by heating with pyridine; the product is 5-(β-acetoxyethyl)-2,2-dicarbethoxyquinuclidine (IV).

Saponification and decarboxylation of the prepared diester (IV) are effected by prolonged boiling (16 hours) with concentrated hydrochloric acid. The resultant 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2 hydrochloride is isolated, after distillation of the hydrochloric acid, in the form of an amorphous, non-crystallizing mass.

Free-5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2 was isolated from the hydrochloride of (V) by two routes: 1) by conversion through the silver salt followed by decomposition of the latter with hydrogen sulfide; 2) by treatment of the hydrochloride with the calculated amount of caustic alkali and extraction of the free acid with anhydrous alcohol from the dry mixture of acid and sodium chloride.

The ethyl ester was obtained by esterification of the hydrochloride of 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2 (V) with an alcoholic solution of hydrogen chloride.

EXPERIMENTAL

Condensation of 3-(β-acetoxyethyl)-4-methylpyridine with dihydoxymalonic ester. A mixture of 20 g 3-(β-acetoxyethyl)-4-methylpyridine, 21.3 g dihydroxymalonic ester and 65 ml acetic anhydride was heated 10 hours on a boiling water bath. The resultant solution was evaporated in vacuum on a boiling water bath, and the residue was distilled at 0.2 mm. Two fractions were collected: 1st 110-142°, 8.18 g; 2nd 180-200°, 19.7 g.

The 1st fraction was mainly the original 3-(β-acetoxyethyl)-4-methylpyridine. The 2nd fraction was a mixture of two compounds: 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine (I) and 2-carbethoxymethyl-3,4-(3',4'-pyridino)-dihydropyran (VIb).

Tests showed that a non-crystallizing oily deposit was obtained on treatment of an ethereal solution of the 2nd fraction with the calculated amount of an alcoholic solution of hydrogen chloride; by fractional separation of the hydrochloride it was found possible to isolate two crystalline substances. The following procedure was used for fractional separation. To an ethereal solution of the second fraction was added dropwise a 10% alcoholic solution of hydrogen chloride, and the ethereal-alcoholic solution was decanted from the oily deposit. The latter was triturated with anhydrous ether, whereupon the oil, which had separated after addition of the first 4.5 ml 10% alcoholic solution of hydrogen chloride, crystallized. The crystals melted at 145-147°. Reprecipitation from alcoholic solution with anhydrous ether gave 3.92 g (11%) hydrochloride of 2-dicarbethoxymethyl-3,4-(3',4'-pyridino)-dihydropyran in the form of colorless crystals with m.p. 147-148°. The substance was very soluble in water, soluble in chloroform, methanol and ethanol, poorly soluble in acetone, and insoluble in ether and toluene; it did not give a reaction for the double bond with potassium permanganate.

3.346 mg substance: 6.732 mg CO_2; 1.872 mg H_2O. 3.612 mg substance: 7.282 mg CO_2; 2.010 mg H_2O. 7.162 mg substance: 0.277 ml N_2 (25.5°, 735 mm). 4.335 mg substance: 1.836 mg AgCl. Found %: C 54.87, 54.98; H 6.26, 6.23; N 4.27; Cl' 10.48. $C_{15}H_{19}O_5N \cdot HCl$. Calculated %: C 54.62; H 6.09; N 4.42; Cl' 10.77.

After separation of the hydrochloride of 2-dicarbethoxymethyl-3,4-(3',4'-pyridino)-dihydropyran, addition was made in small portions to the ether-alcohol solution of 1 ml 10% alcoholic hydrogen chloride. An oil came down which did not crystallize when triturated with anhydrous ether and was apparently a mixture of the hydrochlorides of 2-dicarbethoxymethyl-3,4-(3',4'-pyridino)-dihydropyran and 3-(β-acetoxyethyl)-4-β,β-dicarbethoxyvinyl)-pyridine. On further treatment of the ether-alcoholic solution with 15 ml 10% alcoholic hydrogen chloride, the precipitated oily hydrochloride crystallized when rubbed with a glass rod. Reprecipitation from anhydrous alcohol with anhydrous ether brought down 15.05 g (36.1%) hydrochloride of 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine with m.p. 111-112°.

The compound forms colorless needles, very readily soluble in water, methanol, ethanol, acetone and chloroform, insoluble in ether, toluene, benzene and ligroin; it gives a reaction for the double bond with potassium permanganate; on heating with alcoholic hydrogen chloride it forms ethyl acetate and (VIb).

3.579 mg substance: 7.199 mg CO_2; 1.992 mg H_2O. 4.023 mg substance: 8.039 mg CO_2; 2.250 mg H_2O. 7.122 mg substance: 0.235 ml N_2 (21.5°, 752.5 mm). 7.374 mg substance: 0.246 ml N_2 (20°, 757 mm). 4.427 mg substance: 1.713 mg AgCl. 6.575 mg substance: 2.518 mg AgCl. Found %: C 54.86, 54.50; H 6.24, 6.25; N 3.79, 3.88; Cl' 9.58, 9.47. $C_{17}H_{21}O_6N \cdot HCl$. Calculated %: C 54.98; H 5.93; N 3.77; Cl' 9.59.

Picrate: yellow crystals with m.p. 115-116°

Transformation of 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine (I) into 2-dicarbethoxymethyl-3,4-(3',4'-pyridino)-dihydropyran (VIb). 0.5 g hydrochloride of 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine was boiled with 15 ml 8% alcoholic hydrogen chloride for 8 hours. The solution was evaporated to a volume of 2 ml in vacuum and diluted with anhydrous ether; the hydrochloride of 2-dicarbethoxymethyl-3,4-(3',4'-pyridino)-dihydropyran came down in the form of colorless crystals with m.p. 147-148°. Yield 0.44 (99.2%).

6.410 mg substance: 0.247 ml N_2 (25.5°, 735 mm). 4.410 mg substance: 1.901 mg AgCl. Found %: N 4.26; Cl' 10.67. $C_{15}H_{19}O_5N \cdot HCl$. Calculated %: N 4.42; Cl' 10.77

3,4-(3',4'-Pyridino)-dihydropyran-2-acetic acid (VIII). 0.5 g hydrochloride of 2-dicarbethoxymethyl-3,4-(3',4'-pyridino)-dihydropyran was heated with 50 ml 17% hydrochloric acid at the boil for 8 hours. The solution was decolorized with carbon and evaporated in a vacuum. The solid residue was triturated with anhydrous alcohol, filtered, and dried in a vacuum desiccator to give the hydrochloride of 3,4-(3',4'-pyridino)-dihydropyran-2-acetic acid in the form of a white crystalline powder with m.p. 200.5-201.5° (with decomposition). The compound dissolves readily in water, poorly in alcohol, acetone, chloroform and benzene; it is insoluble in ether. Yield 0.34 g (97.6%). The free acid was obtained by treating a solution of 0.15 g of the hydrochloride in 3 ml distilled water with 0.06 g sodium acetate. The precipitate, which came down after standing for 24 hours, was filtered, washed twice with water (3 ml each time) and dried in a vacuum desiccator. Yield 0.1 g (79%) 3,4-(3',4'-pyridino)-dihydropyran-2-acetic acid. Colorless crystals, m.p. 192-194° (with decomposition). No melting point depression in a mixed test with "acid B" obtained by saponification of 3-(β-acetoxyethyl)-4-(γ,γ,γ-trichloro-β-hydroxypropyl)-pyridine [2].

Hydrogenation of 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine. A mixture of 11.1 g 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine hydrochloride, 200 ml anhydrous alcohol and 0.37 g platinum catalyst prepared by Adams' method was hydrogenated at 17-20° under a pressure of 40-50 cm water column.

After absorption of 1 mole hydrogen (0.8 liter), hydrogenation slowed down appreciably. For separation of the intermediate product, 2 ml of the reaction solution was taken. Dilution of the alcoholic solution with anhydrous ether brought down a crystalline precipitate which was reprecipitated from anhydrous alcohol with anhydrous ether; in this way the hydrochloride of 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyethyl)-pyridine was obtained in the form of colorless needles with m.p. 109-110°, readily soluble in water, methanol, ethanol, acetone and chloroform, insoluble in ether. Negative reaction for double bond with potassium permanganate.

3.542 mg substance: 7.094 mg CO_2; 2.089 mg H_2O. Found %: C 54.65; H 6.60. $C_{17}H_{23}O_6N \cdot HCl$. Calculated %: C 54.61; H 6.42.

The main bulk of the reaction mass was subjected to further hydrogenation which was completed in 15 days. The catalyst was filtered off and the filtrate evaporated in vacuum on a boiling water bath to give 11.31 g 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine in the form of a viscous, syrupy oil. Quantitative yield. Part of the compound was dissolved in water and treated with 50% potassium carbonate solution. The separated base was extracted with chloroform; the chloroform solution was dried with potassium carbonate, the chloroform was driven off, and the residue distilled in vacuum (0.3 mm). A fraction boiling at 194-197° was collected. Considerable resinification occurred during the distillation. 3-(β-Acetoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine is a colorless, viscous liquid, readily soluble in organic solvents, poorly in water. Gives an alkaline reaction to phenolphthalein, n_D^{20} 1.4790.

3.317 mg substance: 7.220 mg CO_2; 2.525 mg H_2O. 3.316 mg substance: 7.178 mg CO_2; 2.510 mg H_2O. 9.493 mg substance: 0.321 ml N_2 (22°, 728.0 mm). 10.597 mg substance: 0.365 ml N_2 (20°, 731.0 mm). Found %: C 59.40, 59.07; H 8.52, 8.47; N 3.75, 3.85. $C_{17}H_{29}O_6N$. Calculated %: C 59.47; H 8.46; N 4.08.

The hydrochloride, picrate, picrolonate and reineckate were isolated in the form of non-crystallizing oils.

5-(β-Acetoxyethyl)-2,2-dicarbethoxyquinuclidine (IV). To a solution of 11.3 g 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyethyl)-piperidine in 50 ml dry chloroform was added a solution of 4.76 g bromine in 100 ml dry chloroform with stirring in the course of 9 hours at room temperature. The chloroform was taken off in vacuum and the residue (15.8 g) was dissolved in 50 ml water and treated with 50 ml 50% potassium carbonate solution. 3-(β-Acetoxyethyl)-4-(β,β-dicarbethoxy β-bromoethyl)-piperidine came out as an oil and was extracted with ether. The ethereal solution was evaporated down in vacuum and the residual oil was dissolved in 50 ml dry pyridine. The solution was boiled 2 hours. The pyridine was taken off in vacuum, and the hydrobromide of 5-(β-acetoxyethyl)-2,2-dicarbethoxyquinuclidine was treated with 30 ml 50% aqueous potassium carbonate solution. The separated base was extracted with ether; the ethereal solution was dried with potassium carbonate, the ether was driven off, and the residue was distilled in vacuum (0.5 mm). A fraction boiling at 110-170° was collected. The wide boiling range was due to the compound being in the form of a mixture of diastereoisomers. Much resinification occurred during distillation. Yield 4.6 g 5-(β-acetoxyethyl)-2,2-dicarbethoxyquinuclidine or 45.2% of the theoretical.

The compound is a colorless, mobile oil, readily soluble in organic solvents, very poorly soluble in water.

n_D^{20} 1.4809, d_4^{20} 1.133, MR_D 85.63; Calculated 85.21.
4.572 mg substance: 10.082 mg CO_2; 3.439 mg H_2O. 10.040 mg substance: 0.402 ml N_2 (21°, 737.0 mm). Found %: C 60.18; H 8.41; N 4.51. $C_{15}H_{27}O_5N$. Calculated %: C 59.83; H 8.41; N 4.10.

Salts of 5-(β-acetoxyethyl)-2,2-dicarbethoxyquinuclidine with inorganic acids (the hydrochloride, phosphate and sulfate) and with organic acids (benzoate, oxalate), also the picrate, reineckate, methiodide and ethobromide, are isolated in the form of non-crystallizing oils.

5-(β-Hydroxyethyl)-quinuclidinecarboxylic acid-2 (V). A solution of 3.9 g 2,2-dicarbethoxy-5-(β-acetoxyethyl)-quinuclidine in 30 ml concentrated hydrochloric acid was boiled 16 hours. The reaction mass was decolorized with carbon and evaporated to dryness in vacuum. Yield 2.4 g (89.2%) 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2 hydrochloride in the form of an amorphous powder, readily soluble in water, alcohol and concentrated hydrochloric acid.

8.913 mg substance: 5.597 mg AgCl. Found %: Cl' 15.53. $C_{10}H_{17}O_3N \cdot HCl$. Calculated %: Cl' 15.07.

The free acid was isolated by two methods.

I. 0.3 g hydrochloride was treated with 12.7 ml 0.1 N sodium hydroxide solution; the resultant solution was evaporated to dryness in vacuum. The 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2 was separated from the sodium chloride by dissolving in 5 ml anhydrous alcohol. The alcohol was removed in vacuum to leave 0.2 g acid in the form of a very hygroscopic powder, readily soluble in water, alcohol and chloroform, poorly soluble in acetone and ether, insoluble in ligroin.

II. A solution of 1.5 g hydrochloride in 10 ml distilled water was shaken with 3.45 g freshly prepared silver oxide for 5 hours. The reaction mass was then filtered; the silver salt of 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2, contained in the filtrate, was decomposed with hydrogen sulfide. The silver sulfide was filtered off and washed with distilled water. The filtrate and wash liquors were evaporated to dryness in vacuum. Yield 1.02 g 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2.

Ethyl ester of 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2. 2.0 g of hydrochloride and 25 ml 15% alcoholic solution of hydrogen chloride were boiled for 6 hours; the alcohol was then distilled off in vacuum; the residue was dissolved in 25 ml 15% alcoholic solution of hydrogen chloride and heating continued for a further 6 hours. The alcohol was removed in vacuum and the hydrochloride of the ethyl ester of 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2 was treated with 20 ml 50% potassium carbonate solution; the separated base was extracted with ether and the ether solution dried with potassium carbonate. The ether was driven off and the residual oil distilled at 0.26 mm to give a fraction boiling at 102-115°. Yield 0.2 g (10.2%)* ethyl ester of 5-(β-hydroxyethyl)-quinuclidinecarboxylic acid-2 in the form of a colorless, mobile oil, readily soluble in organic solvents, poorly soluble in water.

5.303 mg substance: 12.319 mg CO_2; 4.310 mg H_2O. 4.690 mg substance: 10.818 mg CO_2; 3.890 mg H_2O. 10.148 mg substance: 0.544 ml N_2 (24°, 734 mm). 10.582 mg substance: 0.538 ml N_2 (25°, 734 mm). Found %: C 63.38, 62.95; H 9.09, 9.28; N 5.95, 6.07. $C_{12}H_{21}O_3N$. Calculated %: C 63.43; H 9.25; N 6.16.

The hydrochloride, picrate and methoidide are isolated in the form of non-crystallizing oils.

SUMMARY

1. 5-(β-Hydroxyethyl)-quinuclidinecarboxylic acid-2 was synthesized by a method starting from 3-(β-acetoxyethyl)-4-methylpyridine.

2. It was shown that condensation of 3-(β-acetoxyethyl)-4-methylpyridine with dihydroxymalonic ester gives, apart from 3-(β-acetoxyethyl)-4-(β,β-dicarbethoxyvinyl)-pyridine, a compound which is evidently 2-dicarbethoxymethyl-3,4-(3',4'-pyridino)-dihydropyran.

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S. Ordzhonikidze All-Union Pharmaceutical Chemical Research Institute, Moscow

*According to the literature [4] the esterification of unsubstituted quinuclidinecarboxylic acid-2 proceeds with a low yield.

**T.p. = C. B. Translation pagination.

HALOGEN-SUBSTITUTED HEMIMELLITIC ACIDS

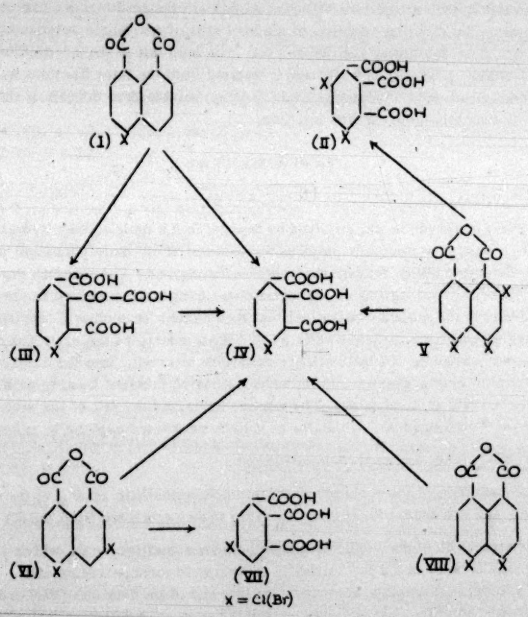
M.M. Dashevsky and G.P. Petrenko

Hemimellitic acid has been known for a long time and a method for its preparation from acenaphthene via naphthalic anhydride was developed by Graebe and Leonhardt [1,2]. We have established that the same route can be followed in order to obtain halogen-substituted hemimellitic acids from the corresponding halogen-substituted naphthalic acids; the latter have been extensively studied and are fully accessible.

Of the halogen-substituted hemimellitic acids, only 4,6-dichlorohemimellitic has so far been described in the literature. It was prepared by oxidation with nitric acid in a sealed tube of the difficultly accessible 1,2,3-trimethyl-4,6-dichlorobenzene [3].

During a study of the structure of polyhalogenated derivatives of acenaphthene we synthesized a series of halogen-substituted naphthalic acids. Their structure was confirmed by oxidation to the corresponding hemimellitic acids; at the same time it was found that the hemimellitic acids were obtained in good yield, some of them from readily accessible halonaphthalic acids.

Below are described the hemimellitic acids that we prepared by oxidation of chloro- and bromonaphthalic acids with aqueous solution of potassium permanganate in an alkaline medium. The method of preparing the starting halonaphthalic acids has been described previously [4].



We obtained both of the possible isomers of monochloro- and monobromohemimellitic acids (IV and VII) and 4,6-dichloro- and 4,6-dibromohemimellitic acids (II).

Oxidation of 4-chloronaphthalic anhydride (I) is accompanied by rupture of the ring from which halogen is absent, and only 4-chlorohemimellitic acid (IV) is obtained. The same acid is formed on oxidation of 4,5-dichloronaphthalic anhydride (VIII).

3,5-Dichloronaphthalic anhydride (VI) gives two acids (IV and VII) on oxidation, in approximately equal amounts. Consequently in this case the migration of halogen from the para-to the meta-position to the carboxyl group does not influence the rate of oxidation of the ring. The two acids (IV) and (VII) are easily separated because 5-chlorohemimellitic acid (VII), like hemimellitic acid itself, gives a sparingly soluble acid monopotassium salt, whereas the potassium salts of 4-chlorohemimellitic acid (IV) are highly soluble in water.

2,4,5-Trichloronaphthalic anhydride (V) likewise forms two acids (II and IV) on oxidation, but in the approximate ratio of 1:2. Consequently the ring containing two chlorine atoms is the more rapidly oxidized. Separation of these two acids from each other is extremely difficult due to their very similar properties. We separated them by repeated fractional precipitation of their lead salts.

We also studied the oxidation of the corresponding bromonaphthalic acids. The latter behave like the chloronaphthalic acids and give similar hemimellitic acids.

Graebe and Guinsbourg [5] also investigated the oxidation of 4-bromonaphthalic acid. They carried the oxidation only as far as the keto acid (III). Oxidation of (III) to bromohemimellitic acid (IV) goes smoothly by the method previously described by Graebe and Leonhardt [1,2] for hemimellitic acid. The mistake of the first-cited authors was in attempting to isolate 4-bromohemimellitic acid in the form of the acid potassium salt which is very soluble in water. Another method had to be developed for isolation of the 4-bromo acid (IV) (see Experimental).

All the chloro- and bromomellitic acids that we studied were obtained in good yield (75-85%) in the form of colorless crystals. Heating to above their melting points converts them into the anhydrides. The latter give nicely crystallizing imides with ammonia.

An interesting feature is the differing solubilities of 5- and 4-halo-substituted hemimellitic acids. The former (VII) are rather poorly soluble in water (about 1-2% at the normal temperature), whereas the 4-halo-substituted derivatives (IV) are soluble in water in the ratio of 1:1. Still less soluble are the acid monopotassium salts of the 5-substituted acids (VII). Also of interest is the differing solubility of the lead salts of 4,6-dihalo-substituted hemimellitic acids (II) in comparison with the monohalo-substituted derivatives (IV). The lead salt of the 4,6-dichloro- acid (II) is more soluble than the salt of the 4-chloro- acid (IV) (X = Cl), and is isolated from the later fractions by fractional precipitation. On the other hand, the lead salt of the 4,6-dibromo- acid (II) is less soluble than the salt of the 4-bromo- acid (IV) (X = Br), and it is therefore separated from the first fractions.

EXPERIMENTAL

Preparation of halosubstituted hemimellitic acids

0.1 mole halonaphthalic anhydride was dissolved by heating in 0.2 mole sodium hydroxide and 300-500 ml water. Into the hot solution was run a previously prepared hot solution of 0.6 mole potassium permanganate in 600 ml water at such a rate that a vigorous but not violent reaction was maintained. The reaction mass was then heated on a water bath for 2 hours with mechanical stirring. If an excess of permanganate remained in the solution, a few milliliters of alcohol was carefully added to the reaction mass, which was then heated for another 5 minutes; it was then filtered hot and the precipitate washed several times with hot water. The filtrate contained the arylglyoxyl dicarboxylic acid, for example (III). To the filtrate was added 0.4 mole sulfuric acid (20% solution). Into the acidified solution was run a hot solution of 0.06 mole potassium permanganate in 75 ml water. After 15 minutes' heating on a water bath, the mass was filtered hot and the residue washed with hot water. The solution contained the salt of the corresponding hemimellitic acid (or acids if oxidation was performed on 3,5-dihalo- or trihalo-substituted naphthalic anhydrides).

Separation of hemimellitic acids from solutions

For the purpose of separation of the 4-chloro- and 4-bromohemimellitic acids (IV) the solution is strongly acidified with hydrochloric acid and evaporated to dryness. The acid is then extracted from the dry residue with ether.

For the purpose of separation of the 5-chloro- and 5-bromohemimellitic acids, which are obtained in admixture with the 4-isomer, advantage is taken of the low solubility of their acid monopotassium salts. The solution of the salts is evaporated to a small volume. On cooling, the monopotassium salt of the 5-isomer (VII) crystallizes out, whereas the salt of the 4-isomer remains in solution. The 4-isomer is isolated from the solution as indicated above. The free acid is got from the potassium salt in the usual manner via the barium salt.

4,6-Dichloro- and 4,6-dibromohemimellitic acids (II), which are obtained together with the 4-chloro- and 4-bromohemimellitic acids respectively, are first separated from the solution in the form of a mixture of acids, as described above for 4-halo-substituted hemimellitic acids; the mixture of free mono- (70%) and dihalo-substituted (30%) acids is then resolved by fractional precipitation of their lead salts; the salt of the 4,6-dichloro- acid (more soluble) comes down from the later fractions, while the lead salt of 4,6-dibromohemimellitic acid (less soluble) comes out of the first fractions.

Preparation of anhydrides and imides of hemimellitic acids

All the hemimellitic acids that we studied were converted into the anhydrides by heating at the melting point.

The acid imides were obtained by heating the corresponding anhydrides with half the quantity of urea for 30 minutes at 160°; the ammonium salt of the imide was thus obtained. Acidification of the latter gave the imide. All the imides that we prepared crystallized nicely from water.

4-Chlorohemimellitic acid (IV). Prepared by oxidation of 4-chloro- or 4,5-dichloronaphthalic anhydride (I or VI). Readily soluble in water; crystallizes from strong hydrochloric acid. M.p. 187-188.5°.

Found %: C 44.02, 44.12; H 1.91, 2.03; Cl 14.45, 14.45. $C_9H_5O_6Cl$. Calculated %: C 44.19; H 2.06; Cl 14.49.

The acid changes to the anhydride when heated to constant weight at 130-145° (15 hours).

Found %: C 47.70, 47.60; H 1.35, 1.35; Cl 15.49, 15.55. $C_9H_3O_5Cl$. Calculated %: Cl 47.70; H 1.33; Cl 15.65.

Imide. M.P. 255.256.5°. Solubility: 100 g aqueous solution at 21° contains 0.1418 g imide.

Found %: C 47.79, 47.95; H 1.77, 1.73; Cl 15.65, 15.70; N 6.17, 6.15. $C_9H_4O_4NCl$. Calculated %: C 47.91; H 1.78; Cl 15.71; N 6.20.

5-Chlorohemimellitic acid (VII). Prepared by oxidation of 3,5-dichloronaphthalic anhydride (VI). Crystallizes from water with 1 molecule of water of crystallization in the form of colorless platelets. Effloresces in the air. M.p. 207°. Solubility in water: 2.03% (at 9°).

Found %: C 44.14, 44.12; H 2.10, 2.03; Cl 14.33, 14.21. $C_9H_5O_6Cl$. Calculated %: C 44.19; H 2.06; Cl 14.49.

Poorly soluble acid monopotassium salt $C_9H_4O_5ClK$: 100 g solution at 7° contains 0.356 g salt.

Anhydride: Found %: C 47.63, 47.55; H 1.37, 1.44; $C_9H_3O_5Cl$. Calculated %: 47.70; H 1.33.

Imide. M.P. 220-221.5°. Solubility: 100 g aqueous solution at 15° contains 0.1469 g imide.

Found %: C 47.83, 47.93; H 1.98, 1.90; Cl 15.71, 15.45; N 6.18, 6.16. $C_9H_4O_4NCl$. Calculated %: C 47.91; H 1.78; Cl 15.71; N 6.20.

4,6-Dichlorohemimellitic acid (II). Prepared by oxidation of 2,4,5-trichloronaphthalic acid (V). Crystallizes from water (1:1) with 2 molecules of water of crystallization. M.p. 226-227°.

Found %: Cl 25.45, 25.36. $C_9H_4O_5Cl_2$. Calculated %: Cl 25.41.

4-Bromohemimellitic acid (IV). Prepared by oxidation of 4-bromonaphthalic anhydride (I). M.p. 198-201°. Readily soluble in water. Crystallizes from 20% aqueous hydrochloric acid, and about $^1/_3$ of the acid taken for crystallization remains in solution.

Found %: C 37.44, 37.36; H 1.64, 1.70; Br 27.86, 27.65. $C_9H_5O_6Br$. Calculated %: C 37.39; H 1.74; Br 27.64.

Silver salt. Found %: Ag 53.54, 53.30. $C_6H_2Br(COOAg)_3$. Calculated %: Ag 53.10.

Imide. M.p. 267-268°. Solubility: at 20° 100 g water dissolves 0.174 g imide.

Found %: C 40.04, 40.02; H 1.42, 1.75; Br 29.24, 29.38; N 5.20, 5.18. $C_9H_4O_4NBr$. Calculated %: C 40.02; H 1.49; Br 29.59; N 5.18.

5-Bromohemimellitic acid (VII). Prepared by oxidation of 2,4-dibromonaphthalic anhydride (VI). The acid monopotassium salt crystallizes with 2 molecules of water. At 22° 100 g water dissolves 0.77 g salt.

Found %: Br 25.53, 25.50. $C_9H_2O_5BrK$. Calculated %: Br 25.89.

The free acid is sparingly soluble in water (in contrast to 4-bromohemimellitic acid). At 23° 100 g solution contains 1.03 g 5-bromohemimellitic acid. It crystallizes with one molecule of water of crystallization. M.p. 218-221°.

Found %: C 37.24, 37.34; H 1.77, 1.64; Br 27.38, 27.55. $C_9H_5O_6Br$. Calculated %: C 37.39; H 1.74; Br 27.64.

Imide. M.p. 242°.

Found %: C 39.93, 40.02; H 1.43, 1.54; Br 29.45, 29.63; N 5.25, 5.13. $C_9H_4O_4NBr$. Calculated %: C 40.02; H 1.49; Br 29.59; N 5.18.

4,6-Dibromohemimellitic acid (II). Prepared by oxidation of 2,4,5-tribromonaphthalic anhydride (V). Good solubility in water. M.p. 195-197°.

Found %: C 29.42, 29.36; H 0.90, 1.04; Br 43.37, 43.45. $C_9H_4O_6Br_2$. Calculated %: C 29.37; H 1.09; Br 43.43.

Imide. M.P. 275-277°.

Found %: C 30.89, 30.74; H 0.90, 0.84; Br 45.77, 45.66; N 3.95, 4.08. $C_9H_3Br_2O_4N$. Calculated %: C 30.97; H 0.86; Br 45.80; N 4.01.

SUMMARY

1. A series of halogen-substituted hemimellitic acids not previously described in the literature was synthesized: 4-chloro-, 4-bromo-, 4,6-dichloro- and 4,6-dibromohemimellitic acids; their anhydrides and imides were also prepared.

2. It was shown that some of these acids are obtained in good yields from easily accessible halonaphthalic acids.

3. During oxidation of halogen-substituted naphthalic acids, the ring that does not contain halogen undergoes oxidation. If both rings contain halogen atoms, then the ring containing the largest number of halogen atoms is oxidized more quickly.

4. Migration of a halogen atom from the para- to the meta-position to the carboxyl group does not affect the velocity of oxidation of the ring.

5. Of interest is the fact that 4-halo-substituted hemimellitic acids (VI) are very highly soluble in water, whereas the 5-isomers (VII) are poorly soluble in water and crystallize nicely from it. 5-Halogen-substituted acids also give sparingly soluble acid monopotassium salts.

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Odessa Polytechnic Institute

CONFIGURATION AND PROPERTIES OF UNSATURATED ACIDS

III. THE REACTIVITY OF β-[α-FURYL]-ACRYLIC ACIDS AND THEIR ESTERS

A.K. Plisov and A.I. Bykovets

In the preceding communication [1] on the reactivity of geometrically isomeric cinnamic acids it was shown that both the acids themselves and their esters are oxidized and hydrogenated with dissimilar activity; in all cases isocinnamic acid and its propyl ester react more rpadily. Concerning hydrolysis of the esters, this, on the contrary, proceeds more slowly in the case of the ester of allocinnamic (isocinnamic) acid. Thus, in these reactions the influence of the configuration of cinnamic acids and their esters is manifested with perfect clarity, in each case under the usual range of conditions.

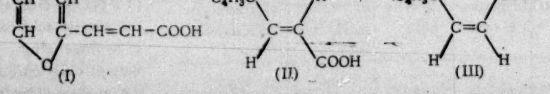
In a study of these and analogous reactions of other unsaturated acids, we had likewise established the influence of composition and structure of the alcohol radical upon the reactivity of the corresponding esters [2].

Continuing the studies that we had initiated on the influence of the configuration of geometrically isomeric unsaturated acids on their reactivity, we considered it necessary also to study this problem with respect to the β-[α-furyl]-acrylic acids and their esters, which contain the heterocyclic furan ring.

β-[α-Furyl]-acrylic acid (I) is known in the form of two isomers corresponding to two geometrical configurations. For this reason they are of undoubted interest, in particular from the viewpoint of the possibility of confirming our earlier conclusions about the influence of spatial structure upon reactivity which were reached in a study of the simplest geometrically isomeric heterocyclic acids. Furthermore, we have here an opportunity of establishing the degree of influence of the furan radical at the β-carbon atom at the double bond on the reactions mentioned, and of comparing it with the influence of the phenyl radical in cinnamic acids.

A study of the β-[α-furyl]-acrylic acids, whose configuration has not yet been definitely established, is also of interest for another reason. A very large number of furan derivatives are, as we know, natural antibiotics secreted by plants and animals. It is quite obvious that further study of the properties of furan derivatives is particularly necessary in connection with those numerous investigations which have been carried out in recent years with the objective of establishing the relation between biological action of these compounds and their chemical properties [3].

We have prepared both of the geometrically isomeric β-[α-furyl]-acrylic acids and have synthesized their ethyl esters. After through purification, these four substances were subjected to oxidation and hydrogenation, and the esters also to saponification. All the experiments, repeated many times, fully confirm our earlier conclusions which were reached in a study of other geometrically isomeric acids. It was found that the β-[α-furyl]-acrylic acid with m.p. 141° (known in the literature as "stable" furanacrylic acid or furylacrylic acid) as well as its ethyl ester are oxidized and hydrogenated very much more slowly than allofurylacrylic acid with m.p. 103° ("labile" β-[α-furyl]-acrylic acid) and its ethyl ester; the ethyl ester of the "stable" form, however, is saponified more quickly than the ester of the "labile" form. These experiments thus clearly show that the "stable" furylacrylic acid is the trans-form (II), while "labile" furylacrylic acid is the cis-form (III):



A further point of interest is that the same transformations of cinnamic acids and their esters proceed somewhat differently. Oxidation of the cis- and trans-cinnamic acids and their propyl esters proceeds under similar conditions very much more slowly than those of furylacrylic acids and their ethyl esters. Evidently the phenyl group hinders oxidation to a greater extent than the furyl group. A similar observation is made during simultaneous hydrogenation of the acids. This conclusion is also confirmed by the saponification reactions which we studied. Saponification of the ethyl esters of furylacrylic acids goes considerably faster than that of propyl esters of cinnamic acids.

Below are presented the results that illustrate the quantitative aspect of the problem.

EXPERIMENTAL

Preparation of β-[α-furyl]-acrylic acids and their ethyl esters. The acids were synthesized from furfurylidene-

malonic acid. The latter was obtained by heating equal weights of furfural, malonic acid and glacial acetic acid. Removal of CO_2 from the furfurylidenemalonic acid gave a mixture of the two geometrically isomeric furylacrylic acids. After their resolution and purification by crystallization from benzene, the "stable" β-[α-furyl]-acrylic acid had m.p. 141°, while its "labile" geometrical isomer melted at 103°. The ethyl esters of these two acids were prepared from their silver salts and ethyl iodide. The silver salt of each acid was obtained by treating the acid with $Ca(OH)_2$ solution to form the Ca salt (readily soluble in water), the solution of which was treated with $AgNO_3$ to precipitate the nearly water-insoluble Ag salt of the furylacrylic acid.

The ethyl ester of "stable" β-[α-furyl]-acrylic acid is a light-yellow liquid with b.p. 114° at 100 mm, n_D^{18} 1.5480.

The ethyl ester of labile β-[α-furyl]-acrylic acid, not described in the literature, is a light-yellow, pleasant-smelling liquid with b.p. 82° at 5 mm, n_D^{20} 1.5398. Soluble in alcohol, benzene and acetic acid.

Oxidation of β-[α-furyl]-acrylic acids and their ethyl esters. The oxidant used was an 0.1 N solution of $K_2Cr_2O_7$ in glacial acetic acid. At definite time intervals 5 ml samples were withdrawn from the reaction solutions, and the amount of unreacted oxidant in these samples was quickly determined by the iodometric method. All the experiments were run at 15° in duplicate, using identical weights of isomers. Results are set forth in Table 1.

TABLE 1

Oxidation of β-[α-furyl]-acrylic acids and their esters

Period from start of experiment (in minutes)	Percent reacted oxidant			
	Furylacrylic acid		Ethyl furylacrylate	
	"stable"	"labile"	"stable"	"labile"
2	–	8	–	–
4	–	20	–	–
5	6	–	0.5	6
6	–	30	–	–
8	–	32	–	–
15	–	–	2.5	12
30	17	–	8.5	18
60	30	100	13	25
90	40	–	–	–
120	–	–	22	44
300	61	–	–	–
420	70	–	–	–

Special experiments established that the product of oxidation in all cases was furfural.

The data of Table 1 not only confirm the results of oxidation of other geometrically isomeric unsaturated acids, but also reveal a very considerable difference in reactivity of furylacrylic acids such as had not previously been observed in the oxidation of other geometrically isomeric unsaturated acids. Concerning the oxidation of esters of furylacrylic acids, it goes more slowly that that of the acids themselves, but again there is a considerable difference in the reactivity of the two forms.

Hydrogenation of β-[α-furyl]-acrylic acids and their ethyl esters. Experiments on the simultaneous hydrogenation of identical weights of the two isomers at 20° were performed as described previously [4]. Results of hydrogenation are set forth in Table 2.

TABLE 2

Hydrogenation of β-[α-furyl]-acrylic acids and their ethyl esters

Duration of hydrogenation (in minutes)	Percent absorption of hydrogen				
	Trans-cinnamic acid	"stable" furylacrylic acid	Allofuryl-acrylic acid	Ethyl ester of "stable" furylacrylic acid	Ethyl ester of allofuryl-acrylic acid
10	3	2	3	4	10
20	6	4	5	10	20
30	8	6	9	14	23
60	16	16	19	18	28
120	24	25	38	25	40
180	40	46	56	31	48
240	46	50	70	38	52
360	70	75	88	46	60
480	78	85	100	60	80

All these experiments were run with Pd catalyst from the same batch, thus making possible a comparison of the activity of "stable" furylacrylic acid and trans-cinnamic acid. As we see from Table 2, the presence of a phenyl radical at the β-carbon atom of the acrylic acid causes a certain retardation of hydrogenation. After absorption of the theoretically calculated amount of hydrogen, the product of hydrogenation was examined; it was established that both forms of furylacrylic acid are hydrogenated to β-[α-furyl]-propionic acid which we isolated in the sufficiently pure state with m.p. 58°.

Saponification of ethyl esters of β-[α-furyl]-acrylic acids. An attempt to saponify the esters by the action of alcoholic sodium hydroxide was unsuccessful because saponification was accompanied by consumption of the alkali in other reactions which we did not study further. Saponification in an acid medium was also unsuccessful due to formation of dark-colored solutions which hindered quantitative analyses. We therefore undertook the fermentative

TABLE 3

Saponification of ethyl esters of β-[α-furyl]-acrylic acids

Period from start of experiment (in minutes)	Ethyl ester of "stable" furylacrylic acid				Ethyl ester of "labile" furylacrylic acid			
	Rise in electrical conductivity (percentages of original)	K	Rise in electrical conductivity (percentages of original)	K	Rise in electrical conductivity (percentages of original)	K	Rise in electrical conductivity (percentages of original)	K
	at 25°		at 33°		at 25°		at 33°	
0	–	–	–	–	–	–	–	–
15	38	0.06	42	0.0909	14	0.0200	22	0.0680
25	42	0.04	45	0.0898	16	0.0146	25	0.0461
45	46	0.032	50	0.0898	20	0.0128	45	
90	51	0.03	55	–	28	0.0149	50	0.0420
120	53	–	55	–	33	–	50	–
300	53	–	55	–	37	–	50	–

saponification of the esters.

Pancreatic lipase is known to hydrolyze various esters, and the ethyl esters of higher fatty acids, for example, are hydrolyzed just as easily as fats are split [5].

We selected acetone with a small water content as the solvent. Experiments on the simultaneous hydrolysis of identical weights of esters were run (in a thermostat) at 25 and 33°. The course of hydrolysis in presence of pancreatin, taken in the amount of 15% of the weight of ester, was followed from the change in electrical conductivity of the solution placed in a cell fitted with platinum electrodes. The electrical conductivity was measured with a resistance bridge with a lamp-optical indicator.

Results of observations of the course of saponification are set forth in Table 3. K is calculated from the formula $K = \frac{2,303}{t} \log \frac{b - a_0}{b - a_t}$, where t is the period from the start of the experiment, a_0 – is the initial electrical conductivity, b is the final electrical conductivity, and a_t – is the electrical conductivity at a given instant.

SUMMARY

1. The properties of the ethyl ester of the "labile" form of β-[α-furyl]-acrylic acid, synthesized for the first time, are described.

2. It is established that the "stable" form of β-[α-furyl]-acrylic acid and its ethyl ester are less reactive in oxidation and hydrogenation reactions than the "labile" form and its ethyl ester; in saponification, on the other hand, the ethyl ester of the "labile" form is the less active.

3. Data are submitted which demonstrate the differing influences of the phenyl and furyl groups on the reactivity of the respective acids and esters.

4. On the basis of the chemical activity the "stable" β-[α-furyl]-acrylic acid and its ethyl ester must be assigned the trans-configuration, and its "labile" form the cis-configuration.

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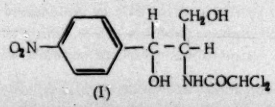
THE CHEMISTRY OF CHLOROMYCETIN (LEVOMYCETIN)

VI. SYNTHESIS OF NEW OPTICALLY ACTIVE ANALOGS OF CHLOROMYCETIN (LEVOMYCETIN)

M.M. Shemyakin, M.N. Kolosov, M.G. Karapetyan, E.M. Bamdas,
Yu.B. Shvetsov, E.I. Vinogradova and L.A. Shchukina

Although in recent years the synthesis has been realized of numerous analogs of D-threo-1-(p-nitrophenyl)-2-dichloroacetylamino-1,3-propanediol (I) (chloromycetin, levomycetin, chloroamphenicol)* and their antimicrobial activity has been investigated, many aspects of the relation between structure and biological activity of this compound are still obscure.



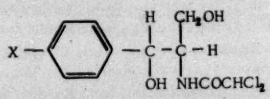
(I)

Still entirely unclarified, for example, is the important question of the cause of the very strong influence on the antimicrobial activity of chloromycetin of the nitro group and of the dichloroacetyl group – two of its important groupings which are extremely rarely encountered in natural compounds. It is still uncertain whether the effect of these groupings is due to their strong polarizing action and whether the latter in association with the spatial configuration of the molecule is one of the main factors governing the high specificity of biological action of chloromycetin.

In our opinion, the answer to these questions can be obtained only after preliminary solution of some subsidiary problems. It is necessary in the first place to establish the influence on the antimicrobial activity of molecules of replacement of the nitro group by diverse electron-accepting and electron-donating groupings of an ionogenic and non-ionogenic character and with a different intensity of polarizing action; second, it is not less important to establish the effect on activity of compounds of the translocation of the nitro group and the dichloroacetyl residue within a system of conjugated double bonds.

A solution of these problems called for the synthesis and study of the antimicrobial activity of a large group of analogs of chloromycetin of previously unknown structure; in this connection it was very important that none of the proposed changes of the chloromycetin molecule should be accompanied by any modifications of its structure. It was particularly necessary that the spatial configuration should remain unchanged in all cases.

The two general methods of preparation of optically active analogs of chloromycetin that we recently developed [1] permitted us relatively easily to realize the synthesis of the projected group of compounds, and up to now we have succeeded in obtaining 25 of the desired analogs, which differ from chloromycetin only in containing, in place of the nitro group, other substituents in the para-position of the benzene ring. Some of these analogs (II-XII) were described in our preceding communications [1]; the others (XIII-XXVI) are described in detail in this paper.



(I): X = NO_2; (II): X = NH_2; (III): X = N_2Cl; (IV): X = Cl; (V): X = I; (VI): X = OH; (VII): X = CN; (VIII): X = COOH; (IX): X = AsO_3H_2; (X): X = 4-$NO_2C_6H_4CH{=}N$; (XI): X = p-$NO_2C_6H_4N{=}N$; (XII): X = 3,4-$(NO_2)(OH)C_6H_3N{=}N$; (XIII): X = SO_2H; (XIV): X = SO_2CH_3; (XV): X = SO_2Cl; (XVI): X = SO_2NH_2; (XVII): X = SO_3Na; (XVIII): X = CH_3CONH; (XIX): X = C_6H_5CONH; (XX): X = p-$NO_2C_6H_4CONH$; (XXI): X = OCH_3; (XXII): X = = $COOCH_3$; (XXIII): X = $C_6H_5CH{=}N$; (XXIV): X = $C_6H_5N{=}N$; (XXV): X = m-$NO_2C_6H_4N{=}N$; (XXVI): X = p-$OHC_6H_4N{=}N$.

The series of sulfur-containing analogs (XIII-XVII) was synthesized by us after we had succeeded in replacing the

* Translator's note: In United States nomenclature chloromycetin is D-threo-α,α-dichloro-N-[β-hydroxy-α-(hydroxymethyl)-p-nitrophenethyl]-acetamide.

NO_2 group by the SO_2H residue in the chloromycetin molecule. This substitution was realized by one of the previously developed general methods [1], namely: starting from chloromycetin (I), via the corresponding amine (II) and the diazonium salt (III) which could be transformed by the action of H_2SO_3 in presence of copper powder into the sulfinic acid (XIII) in 55% yield. The latter was also used for the synthesis of the remaining sulfur-containing analogs of chloromycetin. Thus, interaction of the silver sulfinate with methyl iodide gave a 65% yield of the methylsulfone (XIV), while saturation of an aqueous solution of the sodium sulfinate with chlorine led to the sulfochloride (XV) in a yield of up to 70%. This compound in turn, by the action of a methanol solution of ammonia, was transformed with 80% yield into the sulfonamide (XVI), while short-period heating of the same sulfochloride with an aqueous solution of silver and sodium acetates gave a 90% yield of the sodium sulfonate (XVII).

In addition to the previously described analogs of chloromycetin [1] – the amine (II), the phenol (VI) and the carboxylic acid (VIII), which are characterized by the presence of ionogenic substituents in the aromatic ring, we realized the synthesis of derivatives of these compounds (XVIII-XXII) containing non-ionogenic groupings in the aromatic ring. Compounds of this type were needed to throw more light upon certain aspects of the relation between structure and antimicrobial activity in this group of substances. The acetyl (XVIII), benzoyl (XIX) and p-nitrobenzoyl (XX) derivatives were obtained in satisfactory yields by acylation of amine (II) with acetic anhydride, benzoyl chloride and p-nitrobenzoyl chloride in aqueous solution in presence of sodium acetate. Serious difficulties arose in the preparation of the methoxyl-containing analog (XXI), which could only be synthesized in 23% yield by methylation of phenol (VI) with dimethyl sulfate in weakly alkaline aqueous solution. The analog containing a carbomethoxyl group (XXII) was readily prepared in good yield by the action of methyl iodide on the silver salt of the carboxylic acid (VIII).

In a study of the relation between structure and antimicrobial activity in a series of analogs of chloromycetin, the necessity arose of synthesizing, apart from the compounds already described [1] (X-XII), several other related substances – the azomethine (XXIII) and the azo compounds (XXIV-XXVI), which were also prepared under conditions similar to those of the synthesis of compounds (X-XII). The azomethine (XXIII) was obtained by condensation of amine (II) with benzaldehyde, and the azo compounds (XXIV) and (XXV) by condensation of the same amine with the appropriate nitroso compounds, while compound (XXVI) was got by coupling the diazotized amine (II) with phenol.

Finally we should like to refer briefly to another question. Recently we gave two examples* to show [1] that the method of synthesis of analogs of chloromycetin proposed by Long and Troutman [2], and extensively used by many investigators, leads to compounds of the threo-series. The correctness of this conclusion has now been further confirmed by another three examples – analogs of chloromycetin containing, in the para-position of the benzene ring, CH_3SO_2-, CN- and CH_3O- groups. In the first case D- and L-threo-isomers were synthesized, in the other two cases the products were racemates obtained by mixing of the synthesized D- and L-threo-isomers,** ; these proved identical with the corresponding analogs of chloromycetin obtained by other investigators [3] by the method of Long and Troutman.

EXPERIMENTAL

1. Preparation of D- and L-threo-XIII (X = SO_2H). 10 g of the hydrochloride of D- or L-threo-amine (II) [1] was dissolved in 30 ml 10% H_2SO_4, cooled to 0-3° and diazotized with a solution of 2.2 g $NaNO_2$ in 3.5 ml water. The resultant suspension of diazonium salt was added in a single portion to a solution of 40-50 g SO_2 in 200 g 25% H_2SO_4 stirred at −10°. The mixture was saturated for 5 minutes with a strong stream of SO_2 and, without interrupting the stirring and the gas stream, gradually addition was made to it in the course of 20-25 minutes of 10 g copper powder [4], while the temperature was held at −10 to −5°. After the violent frothing had ceased, the reaction mass was stirred without cooling for 30 minutes and then filtered. The sulfinic acid was extracted from the aqueous solution with ethyl acetate (7-8 times, 500 ml in all); the extract was dried overnight with Na_2SO_4 and evaporated to a small volume in vacuum in a stream of N_2 at 20-25°. The separated solid substance was filtered, washed first with a little ethyl acetate and then with dichloroethane and ether before drying in vacuum. Yield of sulfinic acid 5.5-6.0 g (53-58%); the compound was sufficiently pure for most synthetic purposes. It was converted into the analytically pure form by rapid recrystallization from glacial acetic acid,*** freeing of the crystals from solvent, and extraction with ether in a Soxhlet for 4-6 hours followed by drying in vacuum.

D-threo-XIII (X = SO_2H): softening point 125-127°; $[\alpha]_D^{23}$ −40.6° (c 2.3 in acetone).
L-threo-XIII (X = SO_2H): softening point 125-126°; $[\alpha]_D^{18}$ +45.2° (c 4.6 in acetone).
Found %: C 38.55; H 3.77; g-equivalent 344. $C_{11}H_{13}O_5NSCl_2$. Calculated %: C 38.61; H 3.83; g-equivalent 342.

2. Preparation of D- and L-threo-XIV (X = SO_2CH_3). To a mixture of 1.0 g technical D- or L-threo-sulfinic acid

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* p-Chloro- and p-iodo-substituted analogs of chloromycetin.

** We have previously [1] described the preparation of the racemic p-cyano-substituted analog of chloromycetin.

*** Prolonged heating with CH_3COOH leads to decomposition of the sulfinic acid.

(XII) and 2 ml water was added 0.25 g $NaHCO_3$; after complete solution a solution of 0.5 g $AgNO_3$ in 0.5 ml water was run in. The silver sulfinate was quickly precipitated. The mixture was well stirred and quickly dried in the dark at 30° in vacuum (0.01-0.05 mm). The resultant dry mixture of salts was thoroughly triturated and shaken 8 hours in the dark with 10 ml methyl iodide; the methyl iodide was then distilled off and the residue extracted with acetone. The extract was filtered and evaporated in a vacuum; the residue was triturated with a little ethyl acetate, filtered, and recrystallized from water. Yield of methyl-sulfone 0.68 g (65%).

D-threo-XIV (X = SO_2CH_3): m.p. 165-166°; $[\alpha]_D^{17}$ +13.2° (c 2.0 in alcohol).
L-threo-XIV (X = SO_2CH_3): m.p. 165-166°; $[\alpha]_D^{19}$ −13.2° (c 1.8 in alcohol).
Found %: C 40.46; H 4.29; N 3.96. $C_{12}H_{15}O_5NSCl_2$. Calculated %: C 40.46; H 4.25; N 3.93.

3. Preparation of D- and L-threo-XV (X = SO_2Cl). To a suspension of 2.0 g technical D- or L-threo-sulfinic acid (XIII) in 20 ml water was added 0.5 g $NaHCO_3$; the solution was filtered and saturated with chlorine. The precipitate was filtered, washed with water, dried in vacuum and recrystallized from dichloroethane. Yield of sulfochloride 1.5 g (68%).

D-threo-XV (X = SO_2Cl): m.p. 128-129°; $[\alpha]_D^{18}$ −34.2° (c 4.7 in acetone).
L-threo-XV (X = SO_2Cl): m.p. 128-129°; $[\alpha]_D^{18}$ +34.9° (c 3.9 in acetone).
Found %: C 35.10, H 2.85; N 3.61. $C_{11}H_{12}O_5NSCl_3$. Calculated %: C 35.07; H 3.21; N 3.72.
DL-threo-XV (X = SO_2Cl): m.p. 139-140° (this compound was prepared from D- and L-threo-XV by mixing them and recrystallizing the mixture from dichloroethane.

4. Preparation of D- and L-threo-XVI (X = SO_2NH_2). To a solution, cooled to −40°, of 1.0 g D- or L-threo-sulfochloride in 2 ml methyl alcohol was added 5 ml liquid ammonia, and the reaction mixture left at room temperature 1-2 hours. The methanol was distilled off in vacuum; the residue was triturated with ethyl acetate, filtered, and recrystallized from water. Yield of sulfonamide 0.78 g (82%).

D-threo-XVI (X = SO_2NH_2): m.p. 164-165°; $[\alpha]_D^{20}$ −27.5° (c 3.7 in acetone).
L-threo-XVI (X = SO_2NH_2): m.p. 164-165°; $[\alpha]_D^{19}$ +27.6° (c 3.0 in acetone).
Found %: C 37.16; H 4.16; N 8.12. $C_{11}H_{14}O_5N_2SCl_2$. Calculated %: C 36.98; H 3.95; N 7.84.
DL-threo-XVI (X = SO_2NH_2): m.p. 146-147° (this compound was prepared from D- and L-threo-XVI by mixing and recrystallization from water).

5. Preparation of D- and L-threo-XVII (X = SO_3Na). To 0.90 g D- or L-threo-sulfochloride (XV) was added a boiling solution of 0.40 g silver acetate and 0.33 g crystalline sodium acetate in 90 ml water. The mixture was shaken without heating for 15-20 minutes, and the solution was filtered and evaporated to dryness in vacuum. The residue was triturated with acetone and filtered. Yield of sufficiently pure sodium sulfonate 0.82 (90%). For analysis the substance was purified by reprecipitation from water with acetone and by crystallization from a small volume of water.

D-threo-XVII (X = SO_3Na): $[\alpha]_D^{18}$ + 8.8° (c 4.9 in water).
L-threo-XVII (X = SO_3Na): $[\alpha]_D^{18}$ −7.4° (c 4.6 in water).
Found %: C 34.93; H 3.32; N 3.48. $C_{11}H_{12}O_6NSCl_2Na$. Calculated %: C 34.75; H 3.18; N 3.68.

6. Preparation of D- and L-threo-XVIII (X = CH_3CONH). To a stirred and ice-cooled solution of 3.0 g hydrochloride of D- or L-threo-amine (II) and 1.5 g crystalline sodium acetate in 10 ml water was added dropwise in the course of 10 minutes 1.0 g acetic anhydride. The mixture was stirred for another 30 minutes and left at 0-5° for 1-2 hours, after which the crystals of the substantially pure acetyl derivative were filtered off. The mother liquor was evaporated in vacuum to dryness; the residue was extracted with dry acetone, the solvent distilled off, and the compound recrystallized from water. Total yield 2.36 g (77%).

D-threo-XVIII (X = CH_3CONH): m.p. 164-165°; $[\alpha]_D^{14}$ −29.2° (c 2.8 in acetone).
L-threo-XVIII (X = CH_3CONH): m.p. 164-165°; $[\alpha]_D^{14}$ +27.7° (c 3.6 in acetone).
Found %: C 46.77; H 5.05. $C_{13}H_{16}O_4N_2Cl_2$. Calculated %: C 46.58; H 4.81.
DL-threo-XVIII (X = CH_3CONH): m.p. 199-200° with decomposition (this compound was prepared from D- and L-threo-XVIII by mixing, followed by recrystallization from water.

7. Preparation of D-threo-XIX (X = C_6H_5CONH). To a stirred and ice-cooled solution of 4 g hydrochloride of D-threo-amine (II) and 2 g crystalline sodium acetate in 15 ml water was added 1.5 ml benzoyl chloride in the course of 10 minutes; the reaction mass was then stirred at 0-5° for another hour. The precipitate of benzoyl derivative was filtered and recrystallized from 15% alcohol; yield 2.6 g (54%). Before analysis it was recrystallized from 95% alcohol.

D-threo-XIX (X = C_6H_5CONH): m.p. 181-182°; $[\alpha]_D^{18}$ −30.0° (c 2.0 in acetone).
Found %: C 54.51; H 4.88; N 7.07. $C_{18}H_{18}O_4N_2Cl_2$. Calculated %: C 54.44; H 4.57; N 7.05.

8. Preparation of D-threo-XX (X = p-$O_2NC_6H_4CONH$). 2 g hydrochloride of D-threo-amine (II) and 1 g potassium

acetate were dissolved in 7 ml water, the solution was cooled to 3-5° and addition was made with vigorous stirring of a solution of 1.2 g p-nitrobenzoyl chloride in 1.5 ml ethyl acetate. Stirring at 3-5° was continued for 30 minutes and the reaction mass was left one hour at room temperature. The yellow precipitate was filtered and washed with water. Yield of p-nitrobenzoyl derivative 3.6 g (95%). It was purified by recrystallization from alcohol and then from ethyl acetate.

D-threo-XX (X = p-$O_2NC_6H_4CONH$): m.p. 203-204° with decomposition; $[\alpha]_D^{26}$ −29.3° (c 1.0 in acetone). Found %: C 48.64; H 3.87; N 9.22. $C_{18}H_{17}O_6N_3Cl_2$. Calculated %: C 48.87; H 3.84; N 9.50.

9. Preparation of D- and L-threo-XXI (X = OCH_3). Into a mixture of 10 g D- or L-threo-phenol (VI) [1], 10 g dimethyl sulfate, and 80 ml water was run gradually, with energetic shaking at 25-30°, a solution of 3 g NaOH in 60 ml water; the rate of addition of the alkali was regulated in accordance with the rate of neutralization (external indicator – phenolphthalein). The small, residual oil-containing deposit was filtered off; the filtrate was made alkaline with 5% NaOH and extracted with ethyl acetate (6 times with 25 ml each). The extract was washed 3 times with 0.5% NaOH, then with water, and dried with Na_2SO_4 in presence of active carbon. The solvent was removed in vacuum and the residue dissolved in 15 ml dichloroethane; into the solution was gradually run 15-20 ml heptane (in 2-3 ml portions). The first fractions were usually difficultly crystallizing oils and it was necessary to subject them to a second fractional precipitation, whereas the later fractions were sufficiently pure and were quickly recrystallized. Yield of methoxy compound with m.p. 95-98° 2.4 g (23%). The compound was further purified by recrystallization from a mixture of dichloroethane and heptane (1:1), and then from water.•

D-threo-XXI (X = OCH_3): m.p. 101-102°; $[\alpha]_D^{26}$ −34.2° (c 2.0 in acetone).
L-threo-XXI (X = OCH_3): m.p. 101-102° $[\alpha]_D^{14}$ +33.2° (c 2.6 in acetone).
Found %: C 46.76; H 4.99; N 4.59. $C_{12}H_{15}O_4NCl_2$. Calculated %: C 46.75; H 4.87; N 4.54.

DL-threo-XXI (X = OCH_3): m.p. 107.0-107.5° (this compound was obtained from D- and L-threo-XXI by mixing them and then recrystallizing from dichloroethane and then from water).

10. Preparation of D-threo-XXII (X = $COOCH_3$). To a solution of 3.35 g D-threo-acid (VIII) [1] and 0.87 g $NaHCO_3$ in 12 ml water was added a solution of 1.8 g $AgNO_3$ in 2 ml water. The precipitated silver salt was filtered off, washed with alcohol and ether, dried, and (after thorough trituration) shaken for 8 hours with 20 ml methyl iodide. The methyl iodide was then distilled off and the residue extracted 5 times with hot ethyl acetate. The extract was filtered, decolorized by heating with active carbon, and evaporated to dryness in vacuum. Yield of methyl ester 2.8 g (80%). The compound was recrystallized from water.

D-threo-XXII (X = $COOCH_3$): m.p. 128-129°; $[\alpha]_D^{26}$ −29.0° (c 2.4 in acetone).
Found %: C 46.56; H 4.48; N 4.23. $C_{13}H_{15}O_5NCl_2$. Calculated %: C 46.43; H 4.46; N 4.17.

11. Preparation of D- and L-threo-XXIII (X = $C_6H_5CH{=}N$). 5 g hydrochloride of D- or L-threo-amine (II) was dissolved in 30 ml methyl alcohol; to the solution was added 3 g potassium acetate followed by a solution of 1.6 g freshly distilled benzaldehyde in 5 ml methanol. The reaction mixture was left one hour at 20°, heated to the boil and, on cooling, diluted with 150 ml water. The precipitate was filtered, washed with 50% methyl alcohol, dried and triturated with ether. Yield of azomethine 4.13 g (71%). The compound was purified by recrystallization from 50% alcohol.

D-threo-XXIII (X = $C_6H_5CH{=}N$): m.p. 153-154°; $[\alpha]_D^{16}$ −47.5° (c 1.9 in acetone).
L-threo-XXIII (X = $C_6H_5CH{=}N$): m.p. 153-154°; $[\alpha]_D^{15}$ +45.6° (c 2.1 in acetone).
Found %: C 56.59; H 5.11; N 7.47. $C_{18}H_{18}O_3N_2Cl_2$. Calculated %: C 56.72; H 4.76; N 7.35.
DL-threo-XXIII (X = $C_6H_5CH{=}N$): m.p. 146-147° (this compound was prepared from D- and L-threo-XXIII by mixing them and then recrystallizing from 50% alcohol).

12. Preparation of D- and L-threo-XXIV (X = $C_6H_5N{=}N$). To a solution of 6 g hydrochloride of D- or L-threo-amine (II) in 40 ml methyl alcohol was added 1.8 g potassium acetate and a solution of 1.98 g nitrosobenzene in

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• It should be mentioned that an attempt was also made to synthesize D-threo-XXI (X = OCH_3) by another route, namely starting from the previously described D-threo-1-(p-hydroxyphenyl)-2-benzoylamino-1,3-propanediol [1]. Methylation of the latter with dimethyl sulfate in presence of 10% NaOH at 20° gave a 40% yield of D-threo-1-(p-methoxyphenyl)-2-benzoylamino-1,3-propanediol [m.p. 159-160° (from isoamyl alcohol). Found %: C 68.16; H 6.53. $C_{17}H_{19}O_4N$. Calculated %: C 67.77; H 6.31]. Heating of this compound for 1½ hours with 5% HCl followed by extraction with ethyl acetate of the solution (which had been made alkaline) gave a 13% yield of D-threo-1-(p-methoxyphenyl)-2-amino-1,3-propanediol [m.p. 128° (from ethyl acetate). Found %: C 61.00; H 7.34. $C_{10}H_{15}O_3N$. Calculated %: C 60.91; H 7.61]. However, the last step of the synthesis – dichloroacetylation of the prepared aminodiol with the help of $Cl_2CHCOOCH_3$ or $Cl_2CHCOCl$ – could not be realized, since non-crystallizing oily substances were formed.

10 ml glacial acetic acid. The reaction mixture was left 12 hours at 15-20° and then diluted with 150 ml water. A viscous precipitate came down which gradually crystallized after prolonged trituration. It was filtered and twice recrystallized from 30% acetic acid. Yield of azo compound 2.77 g (40%).

D-threo-XXIV (X = $C_6H_5N{=}N$): m.p. 144-145°; $[\alpha]_D^{18}$ −59.1° (c 1.5 in acetone).
L-threo-XXIV (X = $C_6H_5N{=}N$): m.p. 144-145°; $[\alpha]_D^{18}$ + 57.1° (c 1.8 in acetone).
Found %: C 53.40; H 4.91; N 11.27. $C_{17}H_{17}C_3N_5Cl_2$. Calculated %: C 53.42; H 4.47; N 10.98.
DL-threo-XXIV (X = $C_6H_5N{=}N$): m.p. 150-151° (this compound was obtained from D- and L- threo-XXIV by mixing them and then recrystallizing from 30% acetic acid).

13. Preparation of D-threo-XXV (X = m-$O_2NC_6H_4N{=}N$). To a solution of 5.3 g hydrochloride of D-threo-amine (II) in 35 ml methyl alcohol was added a solution of 1.9 g anhydrous sodium acetate in 25 ml methanol and then (with ice cooling) a solution of 2.3 g m-nitrosonitrobenzene in 35 ml glacial acetic acid. The reaction mixture was left for 20 hours at 4-5°, the small precipitate was filtered off and the filtrate poured into 400 ml water. The separated brown oil was washed with water and triturated with benzene, when it soon crystallized. The precipitate of azo compound was filtered and washed with benzene. Yield 5.2 g (76%). On recrystallization of the azo compound from a mixture of alcohol and benzene (1:1) or ethyl acetate and carbon tetrachloride (1:1), it crystallizes with 1.5 molecules of solvent (CCl_4 or C_6H_6), which can be removed by prolonged heating in vacuum.

D-threo-XXV (X = m-$O_2NC_6H_4N{=}N$) + 1.5C_6H_6: m.p. about 100°; $[\alpha]_D^{27}$ −41.2° (c 2.0 in acetone).
Found %: C 57.60; H 4.51; N 10.46; C_6H_6 20.91. $C_{17}H_{16}O_5N_4Cl_2 \cdot 1.5C_6H_6$. Calculated %: C 57.35; H 4.41; N 10.29; C_6H_6 21.51.
D-threo-XXV(X = m-$O_2NC_6H_4N{=}N$) + 1.5CCl_4: m.p. about 100°.
Found %: C 34.07; H 2.50; N 8.78. $C_{17}H_{16}O_5N_4Cl_2 \cdot 1.5CCl_4$. Calculated %: C 33.74; H 2.43; N 8.55.

14. Preparation of D- and L-threo-XXVI (X = p-$OHC_6H_4N{=}N$). 5.0 g hydrochloride of D- or L-threo-amine (II) was dissolved in 65 ml 2.5%HCl and diazotized at 0-5° with a solution of 1.15 g $NaNO_2$ in 5 ml water; the diazo solution was added in the course of 10 minutes to a solution, stirred at 0°, of 1.8 g phenol, 0.75 g NaOH and 3.3 g Na_2CO_3 in 100 ml water. A resinous precipitate quickly came down; it was stirred 1.5-2 hours at 15-20° when it gradually solidified. After 12 hours the solid substance was triturated, washed with a little water, and recrystallized, first from 30% and then from 15% acetic acid. Yield of hydroxyazo compound 3.1 g (52%).

D-threo-XXVI (X = p-$HOC_6H_4N{=}N$): m.p. 179-181°; $[\alpha]_D^{18}$ −59.0° (c 1.6 in acetone).
L-threo-XXVI (X = p-$HOC_6H_4N{=}N$): m.p. 179-181°; $[\alpha]_D^{18}$ +57.4° (c 1.8 in acetone).
Found %: C 51.65; H 4.89; N 10.86. $C_{17}H_{17}O_4N_3Cl_2$. Calculated %: C 51.27; H 4.73; N 10.55.
DL-threo-XXVI (X = p-$HOC_6H_4N{=}N$): m.p. 171-172° (this compound was obtained from D- and L-threo- XXVI by mixing them and then recrystallizing from 15% acetic acid).

SUMMARY

In connection with a study of the relation between structure and antimicrobial activity of chloromycetin (levomycetin), the synthesis was effected of a group of its optically active analogs of the type of

$$p\text{-}XC_6H_4CHOHCH(NHCOCHCl_2)CH_2OH$$

The prepared analogs belong to the D- and L-threo- series and contain X = SO_2H, SO_2CH_3, SO_2Cl, SO_2NH_2, SO_3Na, CH_3CONH, C_6H_5CONH, p-$O_2NC_6H_4CONH$, OCH_3, $COOCH_3$, $C_6H_5CH{=}N$, $C_6H_5N{=}N$, m-$O_2NC_6H_4N{=}N$ and p-$OHC_6H_4N{=}N$.

It was further confirmed with the help of several new examples that the method of synthesis of analogs of chloromycetin previously described by Long and Troutman leads to compounds belonging to the threo- series.

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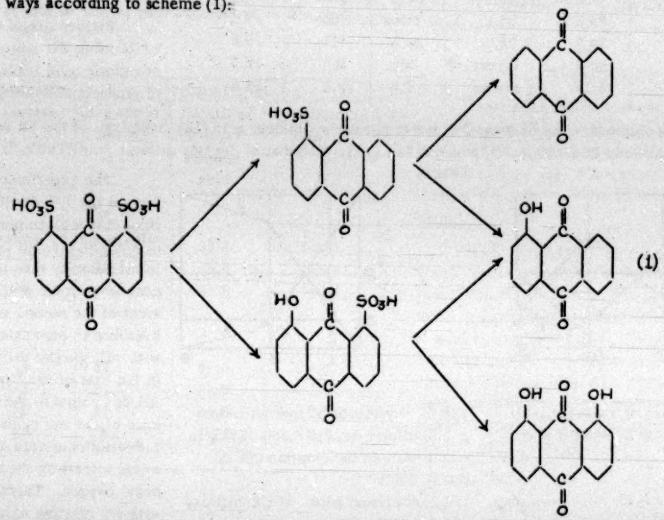
*T.p. = C. B. Translation pagination.

INVESTIGATIONS IN THE ANTHRAQUINONE SERIES

XXV. HYDROLYSIS OF ANTHRAQUINONE-1,8-DISULFONIC ACID*

V.V. Kozlov

Prior to our publications on the hydrolysis of anthraquinone sulfonic acids [1] it was reported that hydrolysis of α,α'-disulfonic acids of anthraquinone was possible at 190-200° only in presence in the sulfuric acid reaction medium (80% H_2SO_4) of mercuric sulfate in the amount of 1-5% by weight of the substance undergoing hydrolysis [2]. We have made a study of the hydrolysis of anthraquinone-1,8-disulfonic acid and its sodium salt. Experiments were performed in sealed tubes with 0.0025 mole substance and 25 ml water or sulfuric acid. The experiments established that hydrolysis of the 1,8-disulfonic acid, first, is possible also in the absence of mercury, and, second, proceeds in various ways according to scheme (1):



(1)

Hydrolysis in 80% sulfuric acid for 6 hours at 230° leads to replacement of one sulfo group by hydrogen with formation of the α-sulfonic acid in a yield of 24.6%. With rising temperature the hydrolysis in the same sulfuric acid progresses to a mixture of products with replacement of the sulfo group not only by hydrogen but also by hydroxyl. Hydrolysis proceeds equally diversely when the concentration of sulfuric acid is changed from 80 to 1% (Table 1).

During hydrolysis in sulfuric acid of high concentration, the hydrogen ion is observed to play an important catalytic role [3], the reaction being so directed that the sulfo groups (one or both) are replaced by hydrogen. On changing over to weak sulfuric acid, however, products of replacement of sulfo groups (one or both) by hydroxyl predominate.

Hydrolysis of the 1,8-disulfonic acid in water goes more completely than in 80% sulfuric acid. Reaction at 230° in water gives after 6 hours up to 35% 1-hydroxy-8-sulfonic acid and 6.5% α-sulfonic acid. At 260° the amount of 1-hydroxy-8-sulfonic acid reaches 75%. The speed and completeness of hydrolysis of 1,8-disulfonic acid increases with increasing duration and dilution (40 ml water for 0.0025 mole substance). Further rise of the temperature of hydrolysis in water (290°) leads to a mixture of products of replacement of the sulfo groups by hydroxyl and hydrogen in

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* Communication XXIV: J. Gen. Chem., 25, 997 (1955). (C. B. Translation page 963).

TABLE 1

Influence of concentration of sulfuric acid upon the hydrolysis of anthraquinone-1,8-disulfonic acid (25 ml H_2SO_4, 6 hours, 260°)

Experiment Number	Concentration of H_2SO_4 (in %)	Obtained (in %)				
		Unchanged disulfonic acid	Na-salt of hydroxy-sulfonic acid	Anthraquinone	α-hydroxy anthraquinone	α-sulfuric acid
1	Water	17.2	74.0	1.1	6.0	1.6
2	0.1	None	62.0	17.2	20.2	None
3	0.25	None	98.0	None	None	None
4	0.5	None	86.0	5.5	8.0	None
5	1.0	10.0	83.0	0.2	3.1	3.1
6	5.0	38.7	48.0	3.3	2.7	6.5
7	10.0	72.0	20.0	1.1	None	6.5
8	20.0	64.6	25.0	None	None	9.8
9	30.0	34.5	28.0	20.5	6.1	9.8
10	50.0	68.9	Traces	9.5	2.3	18.0
11	80.0	57.4	Traces	9.5	19.1	14.5

in the form of 1,8-dihydroxyanthraquinone (48%), 1,8-hydroxysulfonic acid (21%) and anthraquinone (30.6%) (Fig. 1). Hydrolysis of the 1,8-disulfonic acid proceeds the most completely and the least diversely in 0.25% sulfuric acid, a quantitative yield of 1-hydroxy-8-sulfonic acid being attained at 260° after 6 hours (Fig. 2). The acid is obtained in high purity with m.p. 253° and does not show a depression of melting point in admixture with the pure substance prepared from anthraquinone-1,8-disulfonic acid by lime fusion [4].

Further rise of temperature while using the same concentration of sulfuric acid leads to a mixture of products of hydrolysis (Table 2).

As we had observed in the hydrolysis of anthraquinone-α-sulfonic acid [10], hydrolysis of the Na salt of the 1,8-disulfonic acid in water or 0.25% H_2SO_4 proceeds less easily than that of the free sulfonic acid (Table 3).

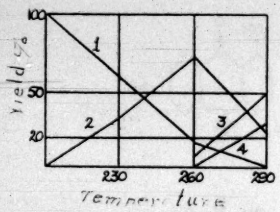


Fig. 1. Hydrolysis of anthraquinone-1,8-disulfonic acid in water in dependence on the temperature (25 ml water, 6 hours).
1) 1,8-disulfonic acid; 2) 1,8-hydroxysulfonic acid; 3) 1,8-dihydroxyanthraquinone; 4) anthraquinone.

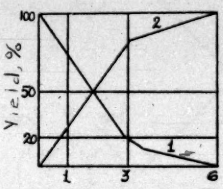


Fig. 2. Hydrolysis of anthraquinone-1,8-disulfonic acid in 0.25% H_2SO_4 in depencence on the duration (25 ml H_2SO_4, 260°).
1) 1,8-disulfonic acid; 2) 1,8-hydroxysulfonic acid;

The experiments on hydrolysis of the 1,8-disulfonic acid show that replacement of one of the sulfo groups by hydrogen or hydroxyl in this sulfonic acid proceeds at a lower velocity than in anthraquinone-α-sulfonic acid. But replacement of the second sulfo group, by hydrogen in particular, proceeds with still greater difficultly than in the case of the first sulfo group. All this points to the non-equivalence of the two sulfo groups in the 1,8-disulfonic acid due to the unequal effects on them of the carbonyl oxygen. This is consistent with the relative value of the velocity constants of the reaction of replacement of one sulfo group by hydrogen and chlorine, as determined by Lauer [2], and the lower yield of chlorosulfonic acid from anthraquinone-1,8-disulfonic acid by comparison with the yields of the analogous products from anthraquinone-1,5-disulfonic acid, which was studied by Krebser [5]. It is interesting to note that transformation of pure 1-hydroxy-8-sulfonic acid, in water and weak sulfuric acid, into α-hydroxyanthraquinone and 1,8-dihydroxyanthraquinone [in accordance with scheme (1)], also proceeds at 260-290°, just as in the case of hydrolysis of the 1,8-disulfonic acid. Hydrolysis of the 1-hydroxy-8-sulfonic acid in 80% sulfuric acid proceeds with destruction of the compound.

Experiments in which the 1,8-disulfonic acid was heated in sealed tubes with weak or concentrated sulfuric acid, with addition of mercuric sulfate, showed that, as in analogous experiments with anthraquinone-α-sulfonic acid, mercury salts promote replacement of the sulfo group by hydrogen (Table 4). The extent of hydrolysis depends on duration, temperature, and concentration of sulfuric acid and mercuric sulfate in the reaction medium. Whereas with 6-hours' heating at 190° in 80% H_2SO_4, without participation of mercury, hydrolysis of the 1,8-disulfonic acid does not occur, in presence of 5% mercuric sulfate (on the weight of sulfonic acid) formation takes place of up to 19% anthraquinone as the product of hydrolysis with replacement of the sulfo group by hydrogen. Hydrolysis in 80% H_2SO_4 with 10% mercuric sulfate at 230° for 6 hours leads to 80% anthraquinone and 11.5% α-sulfonic acid.

Hydrolysis of 1,8-disulfonic acid in 0.25% H_2SO_4 at 260° for 6 hours with 5% mercuric sulfate leads no longer

TABLE 2

Influence of duration on hydrolysis of anthraquinone-1,8-disulfonic acid in weak sulfuric acid
(25 ml 0.25% H_2SO_4, 290°)

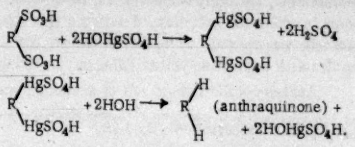
Experiment	Duration (hours)	Obtained (in %)		
		Na salt of hydroxy-sulfonic acid	Anthraquinone	α-Hydroxy-anthraquinone
1	1	91.0	3.1	5.1
2	3	84.0	5.0	11.1
3	6	85.0	5.3	9.3

TABLE 3

Hydrolysis of sodium salt of anthraquinone-1, 8-disulfonic acid in 0.25% H_2SO_4
(25 ml H_2SO_4)

Experiment	Duration (hours)	Obtained (in %)		
		Unchanged disulfonic acid	Na salt of hydroxy-sulfonic acid	α-Sulfonic acid
		For 260°		
1	1	73.2	26.5	None
2	3	70.4	29.0	None
3	6	48.8	51.0	None
		For 290°		
4	1	48.1	48.0	4.1
5	3	37.3	58.0	6.5
6	6	31.6	61.0	8.2
7	12	None	92.0	8.0

to the hydroxysulfonic acid (the sole product of the reaction without mercury), but to its mixture with products of replacement of the sulfo group by hydrogen in the form of anthraquinone, anthraquinone-α-sulfonic acid, and hydroxyanthraquinone. Rise of the concentration of mercury in the aqueous solution of sulfuric acid promotes a rise in concentration of the hydrated salts of mercury which, by reacting with the disulfonic acid directly according to scheme (2) make this reaction predominate over the reaction of direct hydrolysis of $R(SO_3H)_2$ under the action of water alone [6]:



EXPERIMENTAL

Hydrolysis of anthraquinone-1,8-disulfonic acid [7] (m.p. 293.5°; needles; found M 368, calculated M 369) and its sodium salt with water and aqueous sulfuric acid was carried out in sealed tubes (length 250 mm, diameter 20 mm) as described previously [1, 10].

In all experiments 0.0025 mole substance was taken. After hydrolysis the contents of the tube were poured into 50 ml water. The precipitate was filtered, washed on the filter with hot water, dried in a desiccator and weighed. The precipitate in the tube was usually in the form of yellow or slightly brown needles; sometimes, at high working temperatures, it resinified. If the precipitate did not give a coloration with sodium hydroxide solution, its melting point was determined and it was assumed to be

TABLE 4

Influence of mercury upon the hydrolysis of anthraquinone-1,8-disulfonic acid in sulfuric acid (25 ml H_2SO_4, 6 hours)

Experiment Number	Temperature	$HgSO_4$ (in % of sulfonic acid)	Obtained (in %)				
			Unchanged disulfonic acid	Na salt of hydro sulfonic acid	Anthraquinone	α-Hydroxy-anthraquinone	α-Sulfonic acid
For 0.25% H_2SO_4 (554.7 moles water for 1 mole disulfonic acid)							
1	260°	None	None	98.0	None	None	None
2	260	5	None	84.0	6.5	2.5	9.0
For 80% H_2SO_4 (146 moles for 1 mole disulfonic acid)							
3	190°	None	98.0	None	None	None	None
4	190	5	80.0	None	19.0	None	Traces
5	260	None	57.4	Traces	9.5	19.1	14.5
6	260	5	51.0	None	34.4	None	14.5
7*	230	None	77.0	None	Traces	None	18.3
8*	230	10	4.3	None	80.0	None	11.5

* For Na salt.

anthraquinone. When the original precipitate from the alkali solution had a wine-red color, it was treated with 1 N NaOH; the insoluble portion was filtered off, washed on the filter with hot water, dried and weighed. From the known characteristics this portion was identified as anthraquinone. Acidification of the alkaline solution brought down a crystalline precipitate which was filtered, washed on the filter with water, dried in a desiccator and weighed. The product was assumed to be either 1,8-dihydroxyanthraquinone or a mixture of the latter with α-hydroxyanthraquinone.

The dihydroxyanthraquinone isolated in a number of experiments melted at 192° and did not show a depression of melting point in a mixed test with pure 1,8-dihydroxyanthraquinone [8].

The reaction mother liquor, freed from precipitate – a mixture of anthraquinone and hydroxyanthraquinones – was worked up as follows: in the event of a deep wine-red color of the solution with caustic alkalies, pointing to the presence in the solution of anthraquinone-hydroxysulfonic acid, the solution was acidified with a few milliliters of hydrochloric acid and salted out with sodium chloride; in this manner the sodium salt of anthraquinone-1-hydroxy-8-sulfonic acid, sparingly soluble in the cold, came down; it was filtered and dried in a desiccator. In all the experiments in which the 1-hydroxy-8-sulfonic acid was the main reaction product, it was in the precipitate when the hydrolysis tube was opened. In these experiments the 1-hydroxy-8-sulfonic acid was obtained in the form of regular needles with a greenish-yellow color, crystallizing from hydrochloric acid and melting at 256° [9].

Analysis of the sodium salt of anthraquinone-1-hydroxy-8-sulfonic acid:

5.28 mg dry substance: 1.12 mg Na_2SO_4. 4.03 mg dry substance: 0.89 mg Na_2SO_4. Found %: Na 6.85, 7.19. $C_{14}H_7O_6SNa$. Calculated %: Na 7.05.

The mother liquor after removal from it of the sodium salt of the 1-hydroxy-8-sulfonic acid was treated [5] with potassium chlorate for 1 ½ hours at the boil. The resultant chloroanthraquinone was either 1,8-dichloroanthraquinone, formed from 1,8-disulfonic acid which had not reacted during hydrolysis, or α-chloroanthraquinone, formed from the α-sulfonic acid as a product of hydrolysis of anthraquinone-1, 8-disulfonic acid.

The chloroanthraquinone with m.p. 201-203° was assumed to be 1,8-dichloroanthraquinone. It did not show a depression of melting point in admixture with the pure substance. The chloroanthraquinone with m.p. 151-160° was assumed to be α-chloroanthraquinone; it did not show appreciable depression when melted with the pure substance. The chloroanthraquinone melting at 162-200° was assumed to be a mixture of 1,8-dichloroanthraquinone and α-chloroanthraquinone; the percentage content was determined from the melting point curve of an artificial mixture of the pure substances.

Since separate experiments established that the 1-hydroxy-8-sulfonic acid and its sodium salt are completely reduced on treatment with excess of $KClO_3$ in an acid medium at 100°, without formation of products of chlorination, the amount of 1,8-disulfonic acid and α-sulfonic acid could be determined by chlorination of the hydrolysis reaction solution without previous salting-out of the 1,8-hydroxysulfonic acid.

When there was a considerable amount of unreacted 1,8-disulfonic acid after the hydrolysis reaction, the latter crystallized from the reaction solution in the form of needles; recrystallization from 10% HCl gave rhombic crystals with m.p. 292°. The 1,8-disulfonic acid could also be isolated in the form of the sparingly soluble Ba salt, unlike the 1,8-hydroxysulfonic acid whose Ba salt is readily soluble.

The resinification which, as remarked above, occurs in some experiments, must be due to anthraquinone-1-hydroxy-8-sulfonic acid. Heating of the pure substance with water at 290° for 6 hours in a sealed tube leads to 50% unchanged hydroxysulfonic acid, 40% impure dihydroxyanthraquinone and resin. Pure 1,8-dihydroxyanthraquinone and α-hydroxyanthraquinone do not resinify when heated in tubes with water and dilute sulfuric acid.

SUMMARY

1. It was established that anthraquinone-1,8-disulfonic acid can undergo hydrolysis in water and sulfuric acid at 230° and higher in a sealed tube without participation of mercury and with replacement of one or both sulfo groups by hydrogen and hydroxyl, with formation of all the theoretically possible compounds. Mercury salts are capable of leading to products of substitution of the sulfo groups by hydrogen.

2. It was established that the most unidirectional and complete hydrolysis takes place in 0.25% H_2SO_4, a quantitative yield of anthraquinone-1-hydroxy-8-sulfonic acid being attained after 6 hours at 260°.

3. The character of the hydrolysis demonstrates the non-equivalence of the two sulfo groups in anthraquinone-1,8-disulfonic acid, due to the unequal influence of the carbonyl oxygen upon them.

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*T.p. = C. B. Translation pagination.

INVESTIGATIONS IN THE ISOXAZOLE SERIES

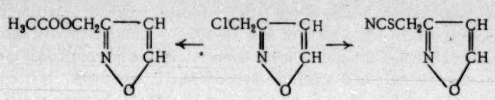
II. REACTIONS OF 3-CHLOROMETHYLISOXAZOLE*

N.K. Kochetkov and A.Ya. Khorlin

A new synthesis of alkyl isoxazoles by condensation of alkyl-β-chlorovinylketones with hydroxylamine was recently reported by us [1]. Utilization in this reaction of chloromethyl-β-chlorovinyl ketone permitted the preparation of chloromethylisoxazole which proved to be the pure γ-isomer. As already indicated [1], the 3-chloromethylisoxazole prepared by this method possesses a rather mobile halogen atom.

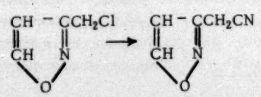
The present paper is devoted to the exchange reactions of the chlorine atom in 3-chloromethylisoxazole which demonstrate the close analogy with the behavior of benzyl chloride and make it a key substance for the synthesis of the difficultly accessible derivatives of isoxazole containing various functional groups in the side chain.

Exchange of the chlorine atom in 3-chloromethylisoxazole for a thiocyano group occurs on heating it with potassium thiocyanate in methanol, a 70% yield of 3-thiocyanomethylisoxazole being obtained; this is a crystalline, fairly stable compound with an unpleasant odor. On heating 3-chloromethylisoxazole with potassium acetate in glacial acetic acid, i.e. under the usual conditions for substitution of reactive halogen, 3-acetoxymethylisoxazole was obtained

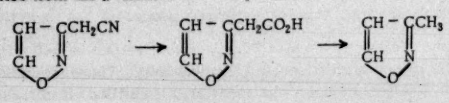


Up to now the conditions have not been established for saponification of the ester to the corresponding isoxazolylcarbinol.

We have reported [1] the preparation of 3-cyanomethylisoxazole by interaction of 3-chloromethylisoxazole with potassium cyanide. It was subsequently found that the use of excess of cyanide in this reaction had a detrimental action. We have now established the optimum conditions for this reaction, enabling 3-cyanomethylisoxazole to be obtained in 68% yield



The perfectly pure nitrile is a crystalline, readily fusible substance. It can be readily saponified to the corresponding isoxazolyl-(3)-acetic acid. Saponification with concentrated hydrochloric acid at room temperature gives the best results, the yield of acid being 86%. Decarboxylation of isoxazolyl-(3)-acetic acid can be accomplished either by pyrolysis or by heating in quinoline; it proceeds, however, with serious resinification and gives a low yield of methylisoxazole. This differentiates isoxazolyl-(3)-acetic acid from other heterocyclic acids of similar structure, for instance α-pyridineacetic acid which is characterized by ease of decarboxylation [2]. The methylisoxazole resulting from the decarboxylation, as shown by the Claisen reaction with potassium alcoholate [3], is pure 3-methylisoxazole and is entirely free from the α-isomer



This confirms the structure of the acid and nitrile and, consequently, once again the structure of the original 3-chloromethylisoxazole.

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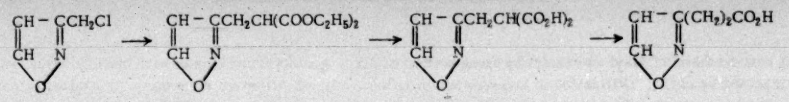
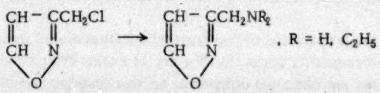
* Communication I see [1].

3-Chloromethylisoxazole could also be made to undergo the malonic synthesis. Under the usual conditions of the reaction, i.e. with addition of the chloro compound to the alcoholic solution of sodium malonic ester, a complex mixture was obtained mainly due to partial decomposition of the isoxazole ring under the relatively drastic conditions of the reaction; this ring is known to be rather unstable toward strong reagents of an alkaline character. Under the reaction conditions employed, however, namely on gradual addition of an alcoholic solution of sodium alkoxide to a mixture of malonic ester and 3-chloromethylisoxzaole in ether, followed by heating of the mixture to 40-60°, the normal reaction product could be obtained – isoxazolyl-(3)-methylmalonic ester – in yield of about 40%. The ester is smoothly saponified with concentrated hydrobromic acid in the cold to the corresponding isoxazolyl-(3)-propionic acid (yield 86%).



In addition to yielding acids of the isoxazole series, 3-chloromethylisoxazole is also a convenient starting point for the synthesis of derivatives of isoxazole containing an amino group in the side chain. This was illustrated by the preparation of 3-dimethylaminomethylisoxazole and 2-aminomethylisoxazole. The first of these compounds was readily prepared by treating 3-chloromethylisoxazole with a twofold excess of diethylamine in an aqueous medium; the isoxazole amine is thus obtained in 78% yield; the latter is a colorless, relatively easily modified liquid; it was characterized by preparation of the picrate.

More difficulties were experienced in the synthesis of 3-aminomethylisoxazole. Amination of 3-chloromethylisoxazole in liquid ammonia is a complex process and gives, in full analogy with the amination of the structurally similar benzyl chloride, a mixture of all three amination products. Reaction of 3-chloromethylisoxazole with hexamethylenetetramine in chloroform gave a 55% yield of the corresponding complex (this again illustrates the high mobility of the chlorine atom); decomposition of the latter, however, proceeds unsatisfactorily, and the hydrochloride of 3-aminomethylisoxazole is obtained in a yield of only 10-15%. 3-Chloromethylisoxazole could be more conveniently aminated with aqueous ammonia solution at room temperature and by continuous saturation of the mixture with gaseous ammonia; in this case the yield of 3-aminomethylisoxazole is about 40%. It is a colorless liquid which changes on storage; the hydrochloride is readily obtained by saturating an ethereal solution of the amine with hydrogen chloride.



The data presented in this paper illustrate the extensive possibilities opened out for the synthesis of various derivatives of isoxazole on the basis of the readily accessible 3-chloromethylisoxazole. It should be noted that derivatives of isoxazole with functional groups in the side chain are attracting attention at the present time in connection with the preparation of a series of physiologically active substances of this series (see, for example, [4, 5].

EXPERIMENTAL

3-Thiocyanomethylisoxazole. Into a hot solution of 9.0 g potassium cyanide in 70 ml methanol is run 7.1 g 3-chloromethylisoxazole, and the reaction mixture is boiled 7 hours in a flask under a reflux condenser. The cooled mixture is run into 150 ml iced water and left for several hours at 3-5°. The crystallizing oil is collected, and dried in a vacuum-desiccator. Recrystallization from ligroin gives colorless needles with m.p. 52-53°. Yield 6.4 g (70%).

Found %: N 19.73, 19.83. $C_5H_4ON_2S$. Calculated %: N 19.99.

3-Thiocyanomethylisoxazole has good solubility in alcohol, acetone, ether and hot benzene; it is less soluble in ligroin, and very poorly soluble in water. It has an unpleasant odor.

3-Acetoxymethylisoxazole. To a hot solution of 36.7 g potassium acetate in 100 ml glacial acetic acid is added 28.5 g 3-chloromethylisoxazole; potassium chloride quickly comes down. The reaction mixture is boiled on an air bath 3 hours and left overnight. The greater part of the acetic acid is distilled off in vacuum, and the residue is carefully neutralized with sodium carbonate and extracted with ether. The extracts are dried over magnesium sulfate, the ether is driven off, and the residue is distilled in vacuum. A fraction is collected with b.p. 95-100° at 13 mm. Yield 19-21 g (55-61%). After redistillation:

B.p. 88-90° at 10 mm, d_4^{20} 1.1922, n_D^{20} 1.4570, MR_D 32.05; Calculated %: 32.04.*

* Here and subsequently in this paper the molecular refraction is calculated on the assumption of a value of

(see following page.)

Found: N 9.69, 9.77. $C_6H_7O_3N$. Calculated %: N 9.86.

3-Acetoxymethylisoxazole is a colorless oil with a pleasant odor; it can be stored for a long time without modification.

3-Cyanomethylisoxazole. Into a hot solution of 85 g potassium cyanide in a mixture of 250 ml alcohol and 150 ml water is run 117.5 g 3-chloromethylisoxazole in large portions in the course of 15 minutes; the reaction mixture boils and deposits potassium chloride. The reaction mixture is boiled 1.5 hours, cooled to room temperature, run into 500 ml water and repeatedly extracted with ether. The extracts are dried over magnesium sulfate, the ether is driven off and the residue distilled in vacuum to give a fraction with b.p. 92-100° at 4 mm. Yield 72.3 g (68%). After two redistillations:

B.p. 87-88° at 3 mm, d_4^{20} 1.1781, n_D^{20} 1.4720, MR_D 25.65; Calculated 25.82. Literature data for 3-cyanomethyl isoxazole [1]; b.p. 91° at 4 mm, n_D^{20} 1.4751.

3-Cyanomethylisoxazole is a colorless liquid with a characteristic odor; on standing it crystallizes completely to colorless crystals with m.p. 15-17°. It can be kept for a long period without change.

Isoxazolyl-(3)-acetic acid. 25 g 3-cyanomethylisoxazole is mixed while cooling with 70 ml concentrated hydrochloric acid, and the reaction mixture is left for 3 days at room temperature. The mixture is saturated with dry hydrogen chloride, the precipitated ammonium chloride is filtered off, the mother liquor is evaporated to dryness in vacuum, and the residue recrystallized from benzene. Colorless needles with m.p. 85-85.5°. Yield 27 g (86%).

Found %: C 47.59, 47.66; H 4.01, 4.10; N 10.95, 10.82. $C_5H_5O_3N$. Calculated %: C 47.25; H 3.97; N 11.01.

Isoxazolyl-(3)-acetic acid has good solubility in water, alcohol and ether; moderate solubility in benzene.

Decarboxylation of isoxazolyl-(3)-acetic acid. A. 8.0 g isoxazolyl-(3)-acetic acid, thoroughly mixed with 0.2 g freshly prepared, finely divided copper, is heated in a Favorsky flask connected to a sloping condenser and immersed in a metal bath. Heavy foaming occurs at 200-210° and the reaction mixture soon resinifies, while a small quantity of colored liquid distils over. The residue in the flask is washed several times with hot ether and the extract is added to the distillate, which is then dried over magnesium sulfate. The ether is driven off and the residue subjected to distillation. Redistillation gives 0.6 g (11%) 3-methylisoxazole with the following constants:

B.p. 118-118.5° at 750 mm, d_4^{20} 1.0183, n_D^{20} 1.4345. Literature data for 3-methylisoxazole [6]: b.p. 118.5°, d_4^{20} 1.022, n_D^{20} 1.435.

A precipitate did not appear even after 10 days on treating the compound in alcohol-ether solution (1:1) with sodium ethoxide at room temperature.

B. In the apparatus described in the preceding experiment was placed a mixture of 9.0 g isoxazolyl-(3)-acetic acid, 15.0 g quinoline and 0.3 g freshly prepared, finely divided copper, and the mixture was slowly heated on a gauze. Violent foaming occured at 200-210°, accompanied by resinification of the mixture, and a small quantity of liquid distilled over. Redistillation gave 1.0 g (13%) 3-methylisoxazole with the following constants: b.p. 118-118.5° at 750 mm, n_D^{20} 1.4340, d_4^{20} 1.0187. The compound likewise does not give a precipitate on treatment with sodium ethoxide.

Isoxazolyl-(3)-methylmalonic ester. In a three-necked flask, fitted with stirrer, reflux condenser with calcium chloride tube and dropping funnel, were put 35.5 g 3-chloromethylisoxazole and 66.0 g ethyl malonate in 100 ml anhydrous ether. To the mixture in the course of 30 minutes was added dropwise a solution of sodium ethoxide prepared from 6.9 g sodium and 100 ml anhydrous alcohol. The mixture heated spontaneously to 40-50° and a precipitate quickly appeared. The reaction mixture was then heated with stirring for 4 hours at 40-50° and 30 minutes on a boiling water bath; a sample taken from the mixture and diluted with water then gave a neutral reaction to phenolphthalein. The mixture was poured into 500 ml water, the oil was separated, the aqueous layer was three times extracted with ether, and the extracts were added to the main portion of the substance which was then dried over magnesium sulfate. The ether was driven off and the residue distilled in vacuum to give a fraction with b.p. 158-164° at 8 mm. After redistillation the b.p. was 150-153° at 5 mm. Yield 29.0 g (40%).

d_4^{20} 1.1577, n_D^{20} 1.4575, MR_D 56.77; Calculated 56.65.
Found %: C 54.46; 54.32; H 6.20, 6.22. $C_{11}H_{15}O_5N$. Calculated %: C 54.76, H 6.27.

Isoxazole-(3)-methylmalonic ester is a colorless, viscous oil which can be stored unchanged for a long time.

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* 2.84 for the nitrogen increment of the isoxazole ring, as previously calculated by us [1]. This leads to considerably better agreement than the previous method of Auwers [6] for calculation of refraction.

Isoxazolyl-(3)-methylmalonic acid. 17.0 g isoxazolyl-(3)-methylmalonic ester was shaken at room temperature with 50 ml concentrated hydrobromic acid until the oily layer had dissolved completely (3-4 days). The reaction mixture was then heated on a bath at a temperature not higher than 30-40°; the solution was evaporated to dryness in vacuum and the residue recrystallized from 15 ml water. The compound forms colorless crystals which decompose without melting at 152-154°. Yield 10.2 g (78%).

Found %: C 45.33, 45.61; H 3.90, 4.04. $C_7H_7O_5N$. Calculated %: C 45.17; H 3.79.

Isoxazolyl-(3)-methylmalonic acid dissolves readily in alcohol, ether and water; it remains unchanged in storage.

β-(Isoxazolyl-3)-propionic acid. 10.0 g isoxazolyl-(3)-methylmalonic ester was boiled 6 hours with 30 ml 20% hydrochloric acid; 50 ml benzene was added; a reflux condenser with a water separator was attached to the flask which was boiled until all the water had been removed. The solvent was driven off from the benzene layer in vacuum and the residue was heated until gas bubbles ceased to come off at 180-190°. After recrystallization of the residue from toluene the substance formed colorless crystals with m.p. 73.5-74°.

Found %: C 51.33, 51.40; H 5.15, 5.12. $C_6H_7O_3N$. Calculated %: C 51.06; H 5.00.

β-Isoxazolyl-(3)-propionic acid dissolves readily in water, alcohol, ether; is poorly soluble in benzene and ligroin.

3-Diethylaminomethylisoxazole. In a three-necked flask, fitted with stirrer, reflux condenser and dropping funnel, was put 180 g 3-chloromethylisoxazole; an equal volume of water was added, followed in the course of 15 minutes with intensive stirring by a solution of 15.0 g diethylamine in 15 ml water. The mixture was then heated with uninterrupted stirring for 45 minutes at 70-80°, the odor of chloromethylisoxazole disappearing completely. The reaction mixture was saturated with potassium carbonate and extracted with ether in a liquid extractor for 20-30 hours. The extract was dried over magnesium sulfate and the residue distilled in vacuum to give a fraction with b.p. 78-80° at 7 mm. After redistillation the b.p. was 66-66.5° at 5 mm. Yield 18.5 g (78%).

d_4^{20} 0.9789, n_D^{20} 1.4534, MR_D 42.61; Calculated 42.07.
Found %: C 62.71, 62.75; H 9.40, 9.18. $C_8H_{14}ON_2$. Calculated %: C 62.24; H 9.15.

3-Diethylaminomethylisoxazole is a colorless oil with a characteristic amine odor, darkening on keeping. Miscible with water and organic solvents.

The picrate is prepared in the usual way in ether; lemon-yellow crystals with m.p. 85-85.5° (from alcohol).

Found %: N 18.18, 18.38. $C_{14}H_{17}O_8N_5$. Calculated %: N 18.10.

3-Aminomethylisoxazole. In a three-necked flask, provided with stirrer, reflux condenser and gas inflow tube, was placed 500 ml saturated aqueous ammonia solution; with intensive stirring 26 g 3-chloromethylisoxazole was quickly run in through the condenser and stirring was continued for another 4 hours while a strong stream of ammonia gas was passed through the reaction mixture for the whole period of the experiment. The mixture was then saturated with potassium carbonate and extracted with ether in a liquid extractor. The extract was dried over magnesium sulfate, the ether was driven off, and the residue was distilled in vacuum to give a fraction with b.p. 85-87° at 12 mm. After redistillation the b.p. was 82° at 10 mm. Yield 9.0 g (43.5%).

d_4^{20} 1.1633, n_D^{20} 1.4900, MR_D 24.38; Calculated 24.67.
Found %: C 48.69, 48.79; H 6.17, 6.58. $C_4H_6ON_2$. Calculated %: C 48.97; H 6.16.

3-Aminomethylisxoazole is a colorless oil with an amine odor; darkens on keeping; miscible with water and organic solvents.

The benzoyl derivative was prepared by shaking 3-aminomethylisoxazole with benzoyl chloride in 10% aqueous sodium hydroxide; the resultant oil quickly crystallized. Colorless platelets with m.p. 102-103° (from benzene-ligroin).

Found %: N 13.56, 14.02. $C_{11}H_{10}O_2N_2$. Calculated %: N 13.85.

The hydrochloride was obtained by saturating a solution of the base in anhydrous ether with dry hydrogen chloride. After recrystallization from anhydrous alcohol, colorless crystals with m.p. 180-182° (with decomposition in a sealed capillary).

Found %: N 21.16, 21.04. $C_4H_7ON_2Cl$. Calculated %: N 20.82.

Complex of 3-chloromethylisoxazole with hexamethylenetetramine. To a solution of 24.0 g hexamethylenetetramine in 250 ml chloroform was added 20.5 g 3-chloromethylisoxazole; the precipitated colorless crystals were filtered after 10 days. M.p. 106-110° (with decomposition). Yield 24.5 g (55%). On attempting to carry out the

decomposition of the complex by the usual method, 3-aminomethylisoxazole hydrochloride was obtained in 10-15% yield.

SUMMARY

1. A study was made of the exchange reactions of the halogen atom in 3-chloromethylisoxazole which demonstrated its high mobility.

2. It was shown that the chlorine atom in 3-chloromethylisoxazole can be replaced by the thiocyano-, the acetoxy- and the cyano- group, by the malonic ester residue, and also by the substituted and unsubstituted amino group.

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Moscow State University

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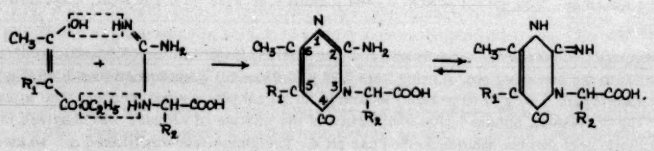
THE SYNTHESIS OF PYRIMIDINE-(N)-ALKYLCARBOXYLIC ACIDS

M.A. Prokofyev and Yu. P. Shvachkin

A few investigations have been carried out on the synthesis and properties of pyrimidine-(N)-alkylcarboxylic acids. These compounds were obtained either by reaction of chloroacetic acid on uracil or its 2-mercapto-derivatives [1] or by condensation of 2-methyl-2-thiocyanopentanone-4 with amino acids [2].

As we showed previously, pyrimidine-(N)-alkylcarboxylic acids are formed by condensation of guanidoaliphatic acids with ethylacetoacetate [3]. In the present work we have extended this reaction to condensation with alkylacetoacetic esters as well as with malonic ester and its derivatives.

Alkylacetoacetic esters are condensed with guanidoacetic and with α-guanidopropionic acid to form the corresponding [4-oxo-2-imino-6-methyl-5-alkyltetrahydropyrimidine-(3)]-alkylcarboxylic acids according to the scheme:



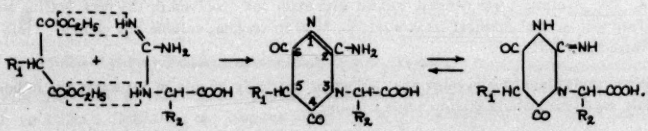
(I) $R_1 = CH_3$, $R_2 = H$; (II) $R_1 = C_2H_5$, $R_2 = H$; (III) $R_1 = C_2H_5$, $R_2 = CH_3$.

The condensation is accomplished by heating the starting substances in alcohol solution in presence of sodium alcoholate. The resultant pyrimidine-(3)-alkylcarboxylic acids are precipitated when the reaction mass is acidified to pH 2-4 (depending on the compound to be isolated), while the unreacted guanido acid remains in solution.

The compounds formed are colorless crystalline substances with high melting points; they are sparingly soluble in water, nearly insoluble in the common organic solvents, but readily soluble in dilute caustic alkalies and in excess of a strong acid.

On reacting with caustic alkalies, pyrimidine-(3)-alkylcarboxylic acids quantitatively bind 1 mole alkali. It may therefore be suggested that in the 2-position of the pyrimidine ring there is apparently not a fixed amino group (because the compound can also exist in the tautomeric imino form).

Malonic ester and its derivatives condense with guanidoacetic and with α-guanidopropionic acids under similar conditions to form the corresponding [4,6-dioxo-2-imino-5-alkylhexahydropyrimidine-(3)]-alkylcarboxylic acids according to the scheme:



(IV) $R_1 = H$, $R_2 = CH_3$; (V) $R_1 = C_2H_5$, $R_2 = H$; (VI) $R_1 = n\text{-}C_4H_9$, $R_2 = H$.

Pyrimidinealkylcarboxylic acids of this type are likewise colorless, crystalline compounds with high melting points, sparingly soluble in water and lower alcohols, insoluble in ether and benzene, readily soluble in dilute caustic alkalies.

A striking feature of these compounds is their strongly marked acidic character which is evidently associated with the mobility of the hydrogen atom in the 5-position of the pyrimidine ring. These compounds are not soluble even in excess of inorganic acids, and on interaction with caustic alkali 1 mole of the substance usually binds more than 1 mole of alkali.

EXPERIMENTAL

1. Preparation of [4-oxo-2-imino-5,6-dimethyltetrahydropyrimidine-(3)]-acetic acid (I). In a three-necked flask, furnished with mechanical stirrer, dropping funnel and reflux condenser with calcium chloride tube, was prepared an alcoholic solution of sodium ethoxide from 1.84 g (0.08 g-atom) sodium and 50 ml anhydrous ethyl alcohol. To the solution was added 2.34 g (0.02 mole) guanidoacetic acid [4]; the mixture was heated to the boil on a glycerol bath; into it was introduced dropwise, with stirring, 8.54 g (0.06 mole) methylacetoacetic ester [5], after which the boiling of the mixture was continued for 4 hours.

The alcohol and the unreacted methylacetoacetic ester were driven off in vacuum, and to the residue was added 5% hydrochloric acid in such quantity that the solution had a pH of 3. The precipitate was filtered off and thoroughly washed with ether; after decolorization with animal charcoal, it was recrystallized from 60 parts of boiling water. Yield 1.2 g (30.5%) colorless substance with m.p. 233°.

The compound is insoluble in cold water, benzene, ether, sparingly soluble in boiling water and in hot methanol and ethanol, readily soluble in dilute caustic alkalies.

Found %: N 21.30, 21.42. $C_8H_{11}O_3N_3$. Calculated %: N 21.31.
For determination of carboxyl a weighed sample was dissolved in a definite excess of the calculated amount of 0.1 N KOH, and the excess of alkali was back-titrated with 0.1 N H_2SO_4 in presence of phenolphthalein. 0.573 g substance: 2.82 ml 0.1 N KOH 0.0464 g substance: 2.32 ml 0.1 N KOH. Calculated ml 0.1 N KOH: 2.86, 2.31.

2. Preparation of [4-oxo-2-imino-6-methyl-5-ethyltetrahydropyrimidine-(3)]-acetic acid (II). The preparation was similar to the preceding one, starting from 2.34 g (0.02 mole) guanidoacetic acid, 15.8 g (0.1 mole) ethylacetoacetic ester [6] and 1.84 g (0.08 g-atom) sodium in 50 ml anhydrous ethyl alcohol. The mixture was heated $4\frac{1}{2}$ hours. The dry residue, obtained after evaporation of the mixture in vacuum, was dissolved in such an amount of 5% hydrochloric acid that the solution formed had pH 4. The precipitate was filtered off, washed with ether, decolorized with animal charcoal, and recrystallized from 70 parts boiling water. Clusters of slender needles from water.

Yield 1.82 g (43.1%). M.p. 245°.

The compound is insoluble in ether, poorly soluble in cold water, readily soluble in hot ethyl alcohol, in boiling water and in dilute caustic alkalies; it dissolves in excess of hydrochloric acid; it again comes down when the hydrochloric acid solution is brought to a pH of 4.

Found %: C 51.01; H 6.45; N 19.93. $C_9H_{13}O_3N_3$. Calculated %: C 51.18; H 6.20; N 19.90.
Carboxyl determination. 0.0775 g substance: 3.44 ml 0.1 N KOH. 0.0440 g substance: 1.99 ml 0.1 N KOH. Calculated ml 0.1 N KOH: 3.65, 2.01.

3. Preparation of α-[4-oxo-2-imino-6-methyl-5-ethyl-tetrahydropyrimidine-(3)]-propionic acid (III). The compound was obtained by the same procedure as above from 2.62 g (0.02 mole) α-guanidopropionic acid [7], 12.64 g (0.08 mole) ethylacetoacetic ester and 1.84 g (0.08 g-atom) sodium in 50 ml anhydrous ethyl alcohol. The mixture was heated 5 hours. The residue after evaporation of the mixture in vacuum was acidified with 5% hydrochloric acid to pH 4. The precipitate was filtered, washed with ether and dissolved in 120 parts boiling water. The solution was decolorized with animal charcoal, evaporated to $\frac{1}{3}$ of its original volume and cooled. Yield 2.52 g (70%) colorless powder with m.p. 215°.

The compound is insoluble in ether and cold water, sparingly soluble in hot water and in boiling ethyl and n-butyl alcohols, readily soluble in dilute caustic alkalies.

Found %: C 53.06; H 6.92; N 18.47. $C_{10}H_{15}O_3N_3$. Calculated %: C 53.32; H 6.71; N 18.66.
Carboxyl determination. 0.0624 g substance: 2.72 ml 0.1 N KOH. 0.0510 g substance: 2.30 ml 0.1 N KOH. Calculated ml 0.1 N KOH: 2.76, 2.27.

4. Preparation of α-[4,6-dioxo-2-iminohexahydropyrimidine-(3)]-propionic acid (IV). The compound was prepared on the same lines as the preceding ones from 2.62 g (0.02 mole) α-guanidopropionic acid, 9.60 g (0.06 mole) malonic ester and 1.84 g (0.08 g-atom) sodium in 50 ml anhydrous ethyl alcohol. Heating was carried out for 5 hours. The dry residue, obtained after removal of alcohol and excess malonic ester in vacuum, was acidified with 5% hydrochloric acid to pH 4. The precipitate was filtered, thoroughly washed with ether, treated with 30 parts warm water and dried at 135°. Yield 2.8 g (70.1%). M.p. 210° (decomposition).

The compound is insoluble in ether and cold water, sparingly soluble in boiling water, readily soluble in dilute caustic alkalies.

Found %: N 20.88, 21.10. $C_7H_9O_4N_3$. Calculated %: N 21.10.

The compound reacts nearly quantitatively with alkali as a dibasic acid.

0.0610 g sub.: 5.83 ml 0.1 N KOH. 0.0555 g sub.: 5.31 ml 0.1 N KOH. *Calculated for interaction with 2 moles caustic alkali ml 0.1 N KOH: 6.06, 5.56.

5. Preparation of [4,6-dioxo-2-imino-5-ethyl-hexahydropyrimidine-(3)]-acetic acid (V). The compound was prepared as above starting from 2.34 g (0.02 mole) guanidoacetic acid, 11.28 g (0.06 mole) ethylmalonic ester [8] and 1.84 g (0.08 g-atom) sodium in 50 ml anhydrous ethyl alcohol. The mixture was heated 4 hours. The residue after evaporation of the mixture was acidified with 5% hydrochloric acid to pH 2. The precipitated compound was filtered, washed with ether and recrystallized from 250 parts boiling water. Yield 1.05 g (23.9%). From water it forms parallelograms with m.p. 213° (decomposition). Insoluble in cold water and ether, difficulty soluble in hot water and hot alcohol, readily soluble in dilute caustic alkalies.

Found %: C 44.90; H 5.63; N 19.88. $C_8H_{11}O_4N_3$. Calculated %: C 45.07; H 5.20; N 19.71.

On interaction with caustic alkali one mole of substance binds about 1.5 moles alkali:

0.0589 g substance: 4.47 ml 0.1 N KOH. 0.0481 g substance: 3.46 ml 0.1 N KOH. Calculated for interaction with 1 mole alkali, ml 0.1 N KOH: 2.68, 2.32.

6. Preparation of [4,6-dioxo-2-imino-5-n-butylhexahydropyrimidine-(3)]-acetic acid (VI). Prepared on same lines from 2.34 g (0.02 mole) guanidoacetic acid, 8.64 g (0.04 mole) n-butylmalonic ester [9] and 1.84 g (0.08 g-atom) sodium in 50 ml anhydrous ethyl alcohol with heating for 5 hours. After evaporation of the mixture in vacuum the residue was acidified with 5% hydrochloric acid to pH 2.

The precipitated product was filtered, washed with ether and recrystallized from 120 parts boiling n-butyl alcohol. Yield 2.2 g (45.6%). Rosettes of curved platelets from n-butyl alcohol. M.p. 210° (decomposition).

The compound is insoluble in cold water and ether, sparingly soluble in boiling water and hot butyl alcohol, easily soluble in dilute caustic alkalies.

Found %: C 49.84; H 6.32; N 17.47. $C_{10}H_{15}O_4N_3$. Calculated %: C 49.78; H 6.27; N 17.42.

On reaction with caustic alkali 1 mole binds approximately 1.5 moles alkali.

0.0543 g substance: 4.10 ml 0.1 N KOH. 0.0445 g substance: 3.23 ml 0.1 N KOH. Calculated for interaction with 1 mole alkali. ml 0.1 N KOH: 2.86, 1.84.

SUMMARY

1. It was shown that guanidoacetic acid and α-guanidopropionic acid can enter into condensation reactions with derivatives of acetoacetic and malonic esters, leading to formation of the corresponding pyrimidine-(N)-alkylc carboxylic acids.

2. The following pyrimidine-(N)-alkylcarboxylic acids, previously undescribed in the literature, were synthesized; [4-oxo-2-imino-5,6-dimethyl-tetrahydropyrimidine-(3)]-acetic acid; [4-oxo-2-imino-6-methyl-5-ethyl-tetrahydropyrimidine-(3)]-acetic acid; α-[4-oxo-2-imino-6-methyl-5-ethyl-tetrahydropyrimidine-(3)]-propionic acid; α-[4,6-dioxo-2-iminohexahydropyrimidine-(3)]-propionic acid [4,6-dioxo-2-imino-5-ethylhexahydropyrimidine-(3)]-acetic acid; and [4,6-dioxo-2-n-butylhexahydropyrimidine-(3)]-acetic acid.

3. It was established that on reaction with caustic alkali [4,6-dioxopyrimidine-(3)-alkylcarboxylic acids bind more than 1 mole alkali, indicating the presence in them of other acidic groups resulting evidently from tautomerism in the pyrimidine ring.

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Moscow State University

SYNTHESES ON THE BASIS OF ANABASINE

XII. HYDROGENATION OF N-(β-PROPIONITRILE)-ANABASINE

E.Kh. Timbekov and A.S. Sadykov

In previous communications data were submitted for the cyanoethylation of anabasine and for the hydrolysis of the product of this reaction. In the present paper we describe the results of a study of the hydrogenation of N-(β-propionitrile)-anabasine.

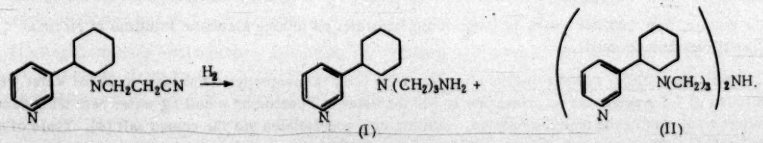
A.P. Terentyev and A.N. Kost developed a fairly simple method of reducing β-aminopropionitriles with metallic sodium containing 2-2.5% potassium in n-butyl alcohol; subsequently, on the basis of the 1,3-diaminopropanes easily obtained in this way, they synthesized a series of urethan derivatives possessing local anesthetic activity [2].

These included piperidine derivatives of the general formula $NCH_2CH_2CH_2NHCOOR$, where R = C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9, iso-C_4H_9, n-C_5H_{11}, n-C_8H_{17}.

Syntheses on the basis of N-(β-propionitrile)-piperidine were carried out by Whitmore and co-workers [3]. These authors obtained γ-(N-piperidyl)-propylamine and di-[γ-(N-piperidyl)-propyl]-amine by hydrogenation of N-(β-propionitrile)-piperidine in presence of nickel catalyst. The new compounds were utilized for synthesis of a series of substances: sulfanilamides, derivatives of 2-aminopyridine, urea, aminotriazines, alloxazine, 8-amino-6-methoxyquinoline and 2,4-diaminopyrimidine.

For the preparation of N-(γ-aminopropyl)-anabasine we used at the start the method of reduction with zinc dust in glacial acetic acid; the yields of the main product of reaction did not exceed 21%. Variation of the concentration of the acetic acid and of the temperature of reduction did not lead to higher yields of the product. Later, therefore, we changed over entirely to a study of the conditions of hydrogenation with hydrogen in presence of Raney nickel catalyst.

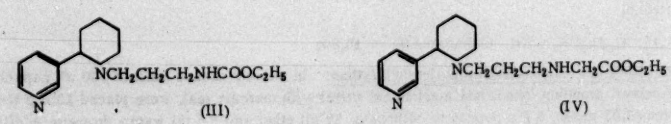
N-(γ-Aminopropyl)-anabasine (I) was obtained side by side with d-[γ-(N-anabasino)-propyl]-amine (II) on hydrogenation of N-(β-propionitrile)-anabasine in an autoclave at 100-125° and an initial hydrogen pressure of 145-150 atm in yields of up to 80%.



The structure of the presumed N-(γ-aminopropyl)-anabasine was verified by oxidation with potassium permanganate; the oxidation product was nicotinic acid.

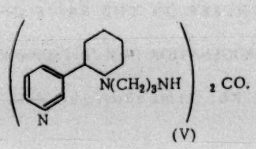
Later we accomplished a number of syntheses at the primary amino group of N-(γ-aminopropyl)-anabasine.

Two products – N-[γ-(N'-anabasino)-propyl]-ethylurethan (III) and the ethyl ester of N-[γ-(N'-anabasino)-propyl]-aminoacetic acid (IV) were obtained by the method previously described for such compounds [2].



Compounds containing the >N – CO-group – lactams, derivatives of urea and barbituric acid – possess

pharmacological properties, which are often very valuable, and have wide practical application; the preparation of N, N'-di-[γ-(N"-anabasino)-propyl]-urea (V) was therefore of interest. We obtained it by condensing N-(γ-aminopropyl)-anabasine with urea.



(V)

EXPERIMENTAL

1. Hydrogenation of N-(β-propionitrile)-anabasine. 77.7 g N-(β-propionitrile)-anabasine was dissolved in 150 ml anhydrous alcohol, saturated at 0° with dry ammonia gas and hydrogenated with hydrogen in presence of 5 g nickel catalyst at 100-125° in a 500 ml autoclave; the calculated amount of hydrogen (1.45 g) was taken up in 45 minutes. The initial hydrogen pressure was 145 atm, the final pressure 70 atm. After cooling, the solution was filtered. The residue after distillation of the alcohol was fractionated in vacuum to give the following fractions: 1st, b.p. up to 165° (1 mm) (5.33 g) – N-(β-propionitrile)-anabasine; 2nd, b.p. 166-170° (1 mm) (31.98 g) – N-(γ-anabasine; on redistillation the main mass of this fraction came over at 166-168° (1 mm); 3rd, b.p. 170-182° (1mm) (37.31 g) – a mixture of N-(γ-aminopropyl)-anabasine and di-[γ-(N-anabasino)-propyl]-amine; the 3rd fraction was dissolved in 250 ml 2 N hydrochloric acid (until acid to Congo red) and then decomposed by addition of 50 ml portions of 2 N sodium hydroxide and extracted with ether. In this manner 6 extracts were obtained. From the first two extracts was isolated di-[γ-(N-anabasino)-propyl]-amine with b.p. 178-180° (1 mm) in the amount of 3.09 g. From the third extract was isolated 3.54 g N-(γ-aminopropyl)-anabasine with b.p. 165-170° (1 mm) and 0.79 g starting mixture with b.p. 170-180° (1 mm). The fourth and fifth extracts and the extract obtained by decomposition of the residue with excess alkali gave 27.52 g N-(γ-aminopropyl)-anabasine with b.p. 166-168° (1 mm).

Two bases were isolated in this way.

a) N-(γ-aminopropyl)-anabasine with b.p. 166-168° (1 mm) in amount of 63.04 g (yield 79.6%).

The picrate, m.p. 228° (decomposition), separates in the form of light-yellow flocs on mixing alcoholic solutions of picric acid and N-(γ-aminopropyl)-anabasine. Crystallizes from alcohol.

Found %: N 18.40, 18.78. $C_{13}H_{21}N_3 \cdot 3C_6H_3O_7N_3$. Calculated %: N 18.54.

b) Di-[γ-(N-anabasino)-propyl]-amine, b.p. 178-180° (1 mm) in amount of 4 g.

The picrate, m.p. 240-241° (with decomposition), separates on mixing alcoholic solutions of picric acid and the base. Crystallizes from alcohol.

2. Oxidation of N-(γ-aminopropyl)-anabasine. 1.0 g N-(γ-aminopropyl)-anabasine in 50 ml water was mixed with a solution of 7.0 g potassium permanganate in 200 ml water and heated on a boiling water bath until decolorized. In the further treatment of the reaction mixture, nicotinic acid was isolated via the copper salt [4]. Yield of nicotinic acid 0.52 g (92%). The compound melted at 229° after recrystallization from hot water. A control mixed sample melted at 229-230°.

3. Acetylation of N-(γ-aminopropyl)-anabasine. 6.0 g N-(γ-aminopropyl)-anabasine was dissolved in 25 ml dry benzene and 5 ml acetic anhydride was added. The mixture was refluxed on a water bath for 4 hours and then decomposed with 10% sodium hydroxide solution and extracted with benzene. The benzene solution was dried over calcined potassium carbonate. The residue after distillation of the solvent was fractionated in vacuum.

N-(γ-Acetylaminopropyl)-anabasine, b.p. 195-196° (1 mm), forms a hydroiodide with m.p. 214°, crystallizing nicely from methyl alcohol.

Found %: N 11.15. $C_{15}H_{23}ON_3 \cdot 2HI$. Calculated %: N 10.80.

4. Preparation of N-[γ-(N'-anabasino)-propyl]-ethylurethan. In a three-necked flask of 200 ml capacity, furnished with reflux condenser, dropping funnel and mechanical stirrer with mercury seal, were placed 10.0 g N-(γ-aminopropyl)-anabasine (0.05 mole), 6.5 g potassium carbonate, 50 ml ether and 2.5 ml water; dropwise addition was made slowly over 4 hours, with ice cooling and vigorous stirring, of 5.0 g (0.05 mole) ethyl chloroformate. The mixture was then further stirred at room temperature for 8 hours, and left for 16 hours. After driving off the ether, the reaction product was extracted with chloroform. The solution was dried over potassium carbonate. After removal of the solvent, the residue was distilled in vacuum.

N-[γ-N'-Anabasino)-propyl]-ethylurethan is a viscous oil with b.p. 210-212° (2 mm), crystallizing after long standing in the form of spangles. Yield 10.85 g (81.7%).

Found %: N 14.30, 14.62. $C_{16}H_{25}O_2N_3$. Calculated %: N 14.42.

5. Preparation of ethyl ester of N-[γ-(N'-anabasino)-propyl]-aminoacetic acid. To a solution of 12.0 g [N-(γ-aminopropyl]-anabasine and 9 g potassium carbonate in 50 ml acetone and 10 ml water was added 7.5 g ethyl chloroacetate. The mixture was refluxed 3 hours on a water bath. The acetone was then distilled off and the residue diluted with 40 ml water and extracted with ether. The ethereal solution was dried over potassium carbonate. The solvent was driven off and the residue distilled in vacuum.

The ethyl ester of N-[γ-(N'-anabasino)-propyl]-aminoacetic acid (yield 4.55 g or 27.3%) is a viscous oil with b.p. 178-180° (0.5 mm); readily soluble in ether and benzene and partly soluble in water. The picrate, m.p. 183-184°, crystallizes from a mixture of alcoholic solutions of the base and picric acid.

Found %: N 17.48, 17.66. $C_{17}H_{27}O_2N_3 \cdot 3C_6H_3O_7N_3$. Calculated %: N 16.93.

The hydrochloride and the hydrobromide separate in the form of oils.

After redistillation in vacuum, the ethyl ester of N-[γ-(N'-anabasino)-propyl]-aminoacetic acid forms crystals with m.p. 191° (from acetone).

1.997 mg substance: 0.291 ml N_2 (30°, 725 mm). 2.147 mg substance: 0.321 ml N_2 (28°, 724 mm). Found %: N 16.13, 16.53.

The compound was not investigated in detail.

6. Condensation of N-(γ-aminopropyl)-anabasine with urea. 8.0 g N-(γ-aminopropyl)-anabasine and 1.0 g urea with a small quantity of crushed glass [3] were refluxed on an oil bath at 140-150° until ammonia ceased to come off (6 hours). The reaction mixture was then distilled in vacuum.

N,N'-Di-[γ-(N"-anabasino)-propyl]-urea is a hygroscopic, vitreous mass with b.p. 166-168° (0.5 mm). Yield 2.01 g (23.7%). The hydrochloride separates as an oil both from alcoholic solutions and from solutions in dry acetone. Prolonged drying in vacuum does not result in crystallization. The hydrobromide and hydroiodide likewise separate as oils from aqueous alcohdic and aqueous acetone solutions. The picrate is a dark-yellow powder, crystallizing with difficulty from water, alcohol, acetone and their mixtures.

SUMMARY

1. Conditions for the hydrogenation of N-(β-propionitrile)-anabasine were investigated. For the first time N-(γ-aminopropyl)-anabasine and di-[γ-(N-anabasino)-propyl]-amine were prepared and characterized.

2. Starting from N-(γ-aminopropyl)-anabasine, the following were prepared for the first time and characterized: N-(γ-acetylaminopropyl)-anabasine; N-[γ-(N'-anabasino)-propyl]-ethylurethan; ethyl ester of N-[γ-(N'-anabasino)-propyl]-aminoacetic acid; and N,N'-di-[γ-(N"-anabasino)-propyl]-urea.

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Central Asian State University

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SYNTHESIS OF COMPOUNDS WITH ANTITHYROID ACTIVITY

IV. PREPARATION OF SOME S-ALKLYLTHIO DERIVATIVES OF IMIDAZOLE WITH THE AID OF BENZOIC ACID ESTERS

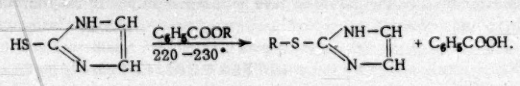
I. B. Simon and I. I. Kovtunovskaya

In the preceding communication [1] we showed the serviceability of synthesis of S-methyl-6-derivatives of thiouracil for the study of the influence of the methyl group at the sulfur in these compounds on the antithyroid activity of the preparation; it was consequently of interest to study the action of S-alkyl and aryl groups on the activity of 2-mercaptoimidazole which itself possesses high activity [2].

Such compounds can be synthesized by the usual method, namely by treating 2-mercaptoimidazole with equimolecular amounts of alkyl halides or aryl halides; in this way halide hydrates are obtained which are decomposed with potassium carbonate; after extraction with anhydrous ethanol, the S-derivatives of 2-mercaptoimidazole crystallize from the solvent. This method is inconvenient due to the low yield of end product.

Jones [3] observed that when the methyl ester of 2 mercaptoimidazole-4(5)-carboxylic acid is melted in a capillary, CO_2 is evolved near the melting point (185-190°) (2-mercaptoimidazole itself is stable even at 250°). S-methylmercaptoimidazole was isolated from the residue. The author considered that the sulfur in the 2-position was alkylated by the ester group due to the facile decarboxylation of an acid of this type. Later he actually obtained S-methyl-2-mercaptoimidazole with the help of methyl benzoate.

Starting from the above observations, we decided to use various esters of benzoic acid for preparation of S-derivatives of 2-mercaptoimidazole. For this purpose we prepared methyl, ethyl, propyl, isopropyl, butyl, isobutyl and benzyl benzoates and reacted 2-mercaptoimidazole with them:



In all cases we obtained the corresponding S-derivatives of 2-mercaptoimidazole. We failed to obtain S-derivatives of thiouracil by this method.

The prepared S-derivatives of 2-mercaptoimidazole and their properties are listed in the table.

Properties of S-derivatives of 2-mercaptoimidazole R–S–C(N–CH)(NH–CH)

Preparation number	R	Empirical formula	Melting point	Yield %	Nitrogen determinations (%)*		Remarks
					Found	Calc'd	
1	CH_3	$C_4H_6N_2S$	142* 139* [7]	40	–	–	Readily soluble in hot water and alcohol; poorly in ether.
2	C_2H_5	$C_5H_8N_2S$	104-105 103-104 [3]	45	–	–	Ditto
3	C_3H_7	$C_6H_{10}N_2S$	112-113	38-39	20.06, 20.16	19.72	Readily soluble in alcohol, poorly in water.
4	iso-C_3H_7	$C_6H_{10}N_2S$	120	35	19.57, 20.05	19.72	Ditto
5	C_4H_9	$C_7H_{12}N_2S$	71	35	17.76, 17.94	17.87	Ditto
6	iso-C_4H_9	$C_7H_{12}N_2S$	85-86	30	17.43, 17.82	17.87	Ditto
7	$CH_2C_6H_5$	$C_{10}H_{10}N_2S$	150	10	14.80, 15.03	14.73	Readily soluble in water and alcohol.

* Analyses were carried out in the microanalytical laboratory under the direction of R. P. Gvirtsman.

EXPERIMENTAL

Acetyl was prepared from acetaldehyde and ethyl alcohol by the previously described method [4]. B.p. 101-103°. Yield 60-62%. Bromoacetal was prepared by Fisher's method [5] by bromination of acetal in presence of calcium carbonate. B.p. 62-63° (15 mm). Yield 50-60%. Aminoacetal was synthesized from bromoacetal and 20% alcoholic ammonia in presence of potassium iodide in an autoclave by the method described by Cass [6] and modified by us. B.p. 161-162°. Yield 45%.

2-Mercaptoimidazole was obtained by our modification of Marckwald's method [7]. 8 g aminoacetal was dissolved in 50 ml dry ether and a current of dry hydrogen chloride was passed. Crystals began to settle at the bottom of the flask. The hydrogen chloride was passed through for 15-20 minutes. The ether was then decanted and addition was made to the precipitate of 8 g potassium thiocyanate dissolved in a small quantity of water; the mixture was refluxed 2 hours on a water bath. The solution was evaporated to dryness and the residue heated on an oil bath at 140° for 2 hours. A little hot water and active carbon were then added and the mass boiled 15 minutes. After filtration the solution was evaporated to a small volume; on cooling crystals came down in the form of needles. Yield 5.0 g (80%). M.p. 226-228°. Marckwald gives 222-223° [7].

Esters of benzoic acid were prepared by boiling the respective alcohols with benzoic acid in presence of concentrated sulfuric acid. Benzyl benzoate was prepared by the Schotten-Baumann benzoylation of benzyl alcohol.

S-derivatives of 2-mercaptoimidazole. In a small flask, fitted with a long air condenser, were mixed equimolecular amounts of 2-mercaptoimidazole and ester of benzoic acid; the mixture was heated on a bath of Wood's metal at 220-230° for an hour. After cooling, the flask contents were extracted with 10% HCl 2-3 times and the solution separated from the resultant semiliquid mass. The aqueous solution was neutralized with sodium carbonate solution. Crystals sometimes came down immediately after neutralization. If crystals did not appear, the solution was evaporated on a water bath to a small volume and cooled. The crystals were recrystallixed from hot water.

SUMMARY

1. Esters of benzoic acid are readily available alkylating agents for 2-mercaptoimidazole.

2. Treatment of 2-mercaptoimidazole with benzoic acid esters gave the corresponding S-derivatives of 2-mercaptoimidazole, of which the following have not been described in the literature: the S-propyl, S-isopropyl-S-butyl-, S-isobutyl and S-benzyl.

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Ukrainian Institute of Experimental Endocrinology

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NEW METHOD OF PREPARATION OF SERINE

I. L. Knunyants and V. V. Shokina

Serine (α-amino-β-hydroxypropionic acid) is one of the most widely distributed of natural amino acids. The known methods for its preparation involve many steps, are laborious, and give low yields.

Thus, on hydrolysis of β-ethoxy-α-aminopropionitrile [1], formed by interaction of glycolaldehyde or ethoxyacetaldehyde with ammonia and hydrocyanic acid, serine is obtained in a yield of 25-40%. A method was recently published [2] for preparation of serine from bromoacetal in 26-30% yield. By formylation of esters of α-acylamino acids, by reduction of formyl derivatives followed by saponification of the resultant esters of β-hydroxy-α-acylamino acids [3-6], serine is obtained in yields of about 10%. King [7, 8], by condensation of acetylaminomalonic ester with formaldehyde, followed by saponification of the ester and decarboxylation of the formed dicarboxylic acid, obtained serine in a yield of up to 65%. Alkylation of phthalimidomalonic ester [5] followed by hydrolysis of the alkyl derivative gave serine in a yield of only 10% reckoned on the bromomalonic ester.

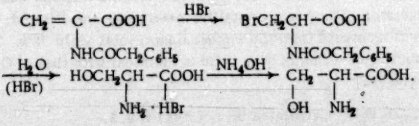
The most widely used is the method involving transformations of esters of acrylic acid [9-13]:

$$CH_2=CHCOOC_2H_5 \rightarrow CH_2BrCHBrCOOC_2H_5 \rightarrow CH_3OCH_2CHBrCOOC_2H_5 \rightarrow$$
$$\rightarrow CH_3OCH_2CHBrCOOH \rightarrow CH_3OCH_2CHNH_2COOH \rightarrow HOCH_2CHNH_2COOH.$$

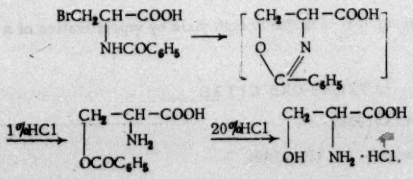
The yield of serine is 30-47%. Mattocks and Hartung [12], using benzylamine instead of ammonia, obtained serine in a yield of 63%, but the synthesis is lengthened by another step.

In the present paper we report on a simple method of preparation of serine and related α-amino-β-hydroxy acids from α-acylamino-unsaturated acids [14].

Hydrogen bromide is added on to α-phenacetylaminoacrylic acid or the α-benzoylaminoacrylic acid to give α-phenacetylamino-β-bromopropionic acid or α-benzoylamino-β-bromopropionic acid. Boiling of α-phenacetylamino-β-bromopropionic acid with very dilute hydrobromic acid gives serine hydrobromide. The free base is separated by the action of concentrated ammonia solution on a solution of the hydrobromide in 80% alcohol. The yield of serine reaches 78% reckoned on the α-phenacetylamino-β-bromopropionic acid and 70.6% reckoned on the α-phenacetylaminoacrylic acid.



For preparation of serine from α-benzoylamino-β-bromopropionic acid, the latter is boiled with 20% hydrochloric acid; the use of more dilute hydrochloric acid results in migration of the nitrogen atom to oxygen with formation of the previously described [15] O-benzoylserine. A similar type of transacetylaction probably occurs through the step of formation of oxazolines.



EXPERIMENTAL

α-Phenacetylamino-β-bromopropionic acid. 20.5 g α-phenacetylaminoacrylic acid was added to 70 ml glacial acetic acid previously saturated with dry hydrogen bromide (18 g HBr). After an hour the whole of the acid had dissolved; the solution was stood at room temperature overnight. The next day the solution was run into 200 ml

iced water. The precipitate was filtered, washed with water until disappearance of the acid reaction to Congo red, and dried. Yield 25.7 g (90%) of substance with m.p. 160-161°. After recrystallization from ethyl acetate, α-phenacetylamino-β-bromopropionic acid melts at 163°; it is readily soluble in alcohol, acetone and dioxan; poorly soluble in ether, heptane, benzene and chloroform; insoluble in cold water. Heating with water leads to cleavage of HBr; the same occurs on treatment with sodium bicarbonate, silver nitrate and pyridine in the cold.

Found %: C 46.8; H 4.4; N 5.1; Br 27.2. $C_{11}H_{12}O_3NBr$. Calculated %: C 46.16; H 4.2; N 4.9; Br 27.9.

α-Benzoylamino-β-bromopropionic acid. Into a suspension of 2 g α-benzoylaminoacrylic acid in 4 ml glacial acetic acid, first redistilled over phosphorus pentoxide, was passed dry hydrogen bromide, likewise dried with phosphorus pentoxide. After 10 minutes the whole of the acid had gone into solution. The hydrogen bromide was passed through until the weight increase was 2.4 g. The solution was poured into 12 ml iced water. The oil which initially separated gradually solidified. The precipitate was filtered and washed with cold water until the acid reaction to Congo had disappeared. Recrystallization from ethyl acetate gave 1.9 g (66%) α-benzoylamino-β-bromopropionic acid with m.p. 136-137° (with decomp.). The acid dissolves readily in alcohol and acetone; it is recrystallized from ether.

An exact amount of the acid was boiled 20 minutes with 0.1 N NaOH solution, the solution was acidified with nitric acid, and halogen was determined by the usual Volhard titration.

Found %: Br 29.2. $C_{10}H_{10}O_3NBr$. Calculated %: Br 29.4.

Preparation of serine. 50 g α-phenacetylamino-β-bromopropionic acid, 300 ml water and 1 ml 40% HBr were heated under a reflux condenser on a water bath until the acid had dissolved; heating was then continued for 3 hours on a gauze. The solution was cooled and the phenylacetic acid was filtered off. The filtrate was extracted with ether for complete removal of the phenylacetic acid. The aqueous solution was evaporated to dryness in vacuum. The residue was dissolved in 60 ml 80% alcohol and addition was made, while cooling with ice, of concentrated solution of ammonia until the odor persisted, and the mass was left overnight in a refrigerator. The finely crystalline precipitate was filtered, washed with anhydrous alcohol and recrystallized from water. Yield 13.1 g serine with m.p. 230° (with decomp.). From the mother liquor was recovered a further 1.4 g serine. Yield 78.5%.

Found %: C 33.51; H 6.59; N 13.47. $C_3H_7O_3N$. Calculated %: C 34.28; H 6.66; N 13.33.

Phenacylation of the serine by the Schotten-Baumann reaction gave N-phenacetylserine with m.p. 130-131° in agreement with the literature value [16]. The identity of our preparation with natural serine was confirmed by paper chromatography.

O-Benzoylserine. 2.7 g α-benzoylamino-β-bromopropionic acid, 15 ml water and 2-3 drops 40% HBr were refluxed at first on a water bath until the acid had dissolved; the solution was then boiled 2 hours on a gauze. The solution was concentrated to 1/5 of its volume in vacuum and extracted with ether for removal of a small amount of benzoic acid. To the aqueous solution was added concentrated ammonia solution until the odor persisted. The mass was left 5-6 hours in a refrigerator. The finely crystalline precipitate was filtered; yield 1 g with m.p. 150°. A further 0.5 g O-benzoylserine was recovered from the mother liquor; total yield 75%. The product gives a positive reaction for α-amino acid with ninhydrin. The melting point is identical with that of O-benzoylserine prepared from 2-phenyl-4-carboxymethyloxazoline [15].

Found %: C 57.07; H 4.99. $C_{10}H_{11}O_4N$. Calculated %: C 57.41; H 5.3.

Serine is prepared from α-benzoylamino-β-bromopropionic acid by boiling with 20% hydrochloric acid for 2 hours.

SUMMARY

A new method is developed for the preparation of serine in high yield by saponification of α-acylamino-β-halopropionic acids.

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Institute of Organic Chemistry of the
Academy of Sciences USSR

*T.p. = C. B. Translation pagination. See C. B. Translation, page 861.
**See C. B. Translation, page 231.

DISCUSSION

THE PAPER BY E. A. UKSHE AND A. I. LEVIN "ON THE COMPOSITION AND PROPERTIES OF THE COMPLEX ELECTROLYTE OF THE COPPER-PYROPHOSPHATE BATH" [1]

I. L. Agafonov

The paper contains the statement: "...ratios of concentrations of $Na_4P_2O_7 : CuSO_4 \leq 2$, should be aimed at since then the nature of the discharging ions will scarcely change, and the lowering of the concentration of free pyrophosphate offers better prospects since in this case crystallization of $Na_4P_2O_7$ on the surface of the cathode becomes improbable [2]. And later: "We have realized in practice such a ratio of concentrations of $CuSO_4$ and $Na_4P_2O_7$ with simultaneous introduction of extraneous complex formers, and this led to fully satisfactory results".

We agreed with the statement of the authors that the nature of the discharging ions when $[Na_4P_2O_7] : [CuSO_4] < 2$ does not change, but at this ratio of concentrations a precipitate of $Na_2Cu_3(P_2O_7)_2$ or CuP_2O_7 is formed and lowers the concentration of discharging complex ions. Consequently a fall in the ratio of $[Na_4P_2O_7] : [CuSO_4]$ is here equivalent to simple dilution of the solution. In the absence of a change in the nature of the discharging ions, it is impossible to obtain in the solution the ratio of concentrations envisaged by the authors. By introducing "extraneous complex formers" the authors actually introduce new complex ions of copper in order to compensate for the loss of copper in solution – naturally at the cost of solution of the precipitate.

The word "precipitate" is not mentioned a single time by the authors, while a precipitate ought to have come down at the ratios of concentrations of $Na_4P_2O_7$ and $CuSO_4$ indicated by them. The precipitate substantially changes the concentration of ions in solution and somewhat complicates the theoretical consideration of the problem of the ionic composition of the solution.

In Table 1, for example, is the remark: "Assumed predominating form: $[Cu(P_2O_7)]^{-2}$" (for the first five lines of the table). Actually at the concentrations employed in electroplating, such an ion will not be present in solution since in the main the reaction goes according to the equation [3]:

$$4CuSO_4 + 4Na_4P_2O_7 = Na_6Cu(P_2O_7)_2 + Na_2Cu_3(P_2O_7)_2 + 4Na_2SO_4. \quad (A)$$

The concentration of copper is thus reduced by a factor of 4, which could certainly lead (although at concentrations very much lower than those cited by the authors in the tables) to the appearance of $[Cu(P_2O_7)]^{-2}$ ions, in appreciable, even if not predominating, amount.

The summary contains the statement: "an inflexion of the curves is observed which corresponds to substantially complete transition of copper into a complex ion". In the text of the paper appears an indication that this situation corresponds to a ratio of $[Na_4P_2O_7] : [CuSO_4] = 3 : 2$. Evidently (assuming the validity of the authors' statement that the solution will then only contain complex ions of $[Cu(P_2O_7)_2]^{-6}$ and $[Cu(P_2O_7)]^{-2}$), this ratio will correspond to the equation:

$$3Na_4P_2O_7 + 2CuSO_4 = Na_6Cu(P_2O_7)_2 + Na_2CuP_2O_7 + 2Na_2SO_4. \quad (B)$$

This ratio thus corresponds not to substantially complete transition of copper to the complex ion but to a 1 : 1 ratio of the concentrations of hexavalent and bivalent complex ions. This ratio is also confirmed by the data of the authors' themselves; indeed they point out that in Fig. 1 the ratio of 3 : 2 for the concentrations of $[Na_4P_2O_7]$ and $[CuSO_4]$ corresponds to point a for which the relative concentrations of the hexa- and bivalent ions are approximately equal to 50% (the curves of relative concentrations of ions of $[Cu(P_2O_7)]^{-2}$ and $[Cu(P_2O_7)_2]^{-6}$) intersect at this point). Moreover, it must be noted that equation (B) is only valid at very low concentrations of electrolytes (10^{-4} molar and less), when precipitate ceases to form and formation of $[Cu(P_2O_7)]^{-2}$ ions becomes possible [3]. At the concentrations considered by the authors, $Na_2Cu_3(P_2O_7)_2$ is precipitated according to the equation:

$$3Na_4P_2O_7 + 2CuSO_4 = \frac{5}{4} Na_6Cu(P_2O_7)_2 + \frac{1}{4} Na_2Cu_3(P_2O_7)_2 + 2Na_2SO4.$$

As we see, the concentrations of the compounds formed bear a fortuitous, or more correctly, an intermediate, character, and do not correspond, contrary to the authors' statement, to "nearly complete transition of copper to the

$[Cu(P_2O_7)_2]^{-6}$ ion", because here a break on the curve of $x = f(C)$, cannot occur. The break obtained by the authors on a curve with only four experimental points is very likely the result of an error of measurements, since some difficulty must arise in measurement of the electrical conductivity in presence of the precipitate formed, so that the operation calls for considerable skill. (Strictly constant conditions must be maintained during formation of the precipitate and its distribution throughout the solution at the instant of measurement, for the conductivity of such a system depends on the form of the particles and on their distribution in the solution. In particular a gross error results from measurement of electrical conductivity without preliminary stirring of the solution, especially when the electrodes are partly immersed in precipitate.)

We did not observe the appearance of any breaks on the isotherms of specific electrical conductivity corresponding to a 3:2 ratio of $[Na_4P_2O_7]$ to $[CuSO_4]$, and in particular at the concentrations cited by the authors: 0.06 M $Na_4P_2O_7$ and 0.04 M $CuSO_4$ [3].

In the light of the foregoing considerations, the authors' statement that the nature of the discharging ions, and consequently also the ionic composition, do not change with decrease in the ratio of $[Na_4P_2O_7]$ to $[CuSO_4]$, although valid, does not follow from the results of the investigation, since at the concentrations required in electroplating the ionic concentration of the solution is governed not so much by the excess of $P_2O_7^{-4}$ ions (the influence of whose concentration on the ionic composition of the solution was considered by the authors) as by the dilution of the solution or the formation of a precipitate when there is a deficiency of these ions (i.e. when $[Na_4P_2O_7]:[CuSO_4]$ is less than 2). In the latter case the concentration of $[Cu(P_2O_7)_2]^{-6}$ ions and the total concentration of copper in the solution are lowered due to separation of the precipitate of $Na_2Cu_3(P_2O_7)_2$. Thus, the authors' suggested fall in the $[Na_4P_2O_7]:[CuSO_4]$ ratio scarcely possesses practical significance, although it would also appear to be required from the condition of prevention of crystallization of $Na_4P_2O_7$ at the cathode, which is detrimental to the electrolytic deposition of copper. By adding sodium citrate (see end of the paper [1]) the authors nevertheless prevented the precipitation but obviously at the cost of partial change of the composition of the discharging ions.

There is another possible method of preventing crystallization of $Na_4P_2O_7$ at the cathode which hinders the increase in cathodic current density during prolonged passage of current due to deterioration of the quality of the copper deposit and lowering of the current yield [2]. This method is the reduction of the pH of the solution, which may be permissible in absence from the solution of SO_4^{-2} ions which lower the practical limit of cementation. This is achieved by using the electrolyte proposed by I. G. Shcherbakov [4] which enables working at lower pH and higher current densities without cementation (absence of the latter is reflected in good ahesion of the deposit) and the other harmful effects mentioned above.

The paper also contains a number of minor errors. The value of $K_H = 2 \cdot 10^{-11}$ cited by the authors as appearing in [5] is actually not mentioned in this source. It is incomprehensible why the author has already given this erroneous reference in three papers (see also [2, 6]). Again, in equation for $E - E^0_{Cu}(2)$ [1] the concentration of $P_2O_7^{-4}$ is calculated as the difference $C^0_{P_2O_7} - C^0_{Cu}$, which is not true at the usual concentrations, again due to separation of a precipitate in accordance with equation (A). Equation (2)[1] (as also the results of the calculation given in Fig. 1 [1]) are evidently only valid at very low concentrations of electrolyte at which a precipitate ceases to come down (about 10^{-4} and less g-ions/liter Cu^{+2}).

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Gorky Polytechnic Institute

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THE PAPER BY E. A. UKSHE and A. I. LEVIN "ON THE COMPOSITION AND PROPERTIES OF THE COMPLEX ELECTROLYTE OF THE COPPER-PYROPHOSPHATE BATH"

V. P. Vasilyev and K. B. Yatsimirsky

In number 5 of "Journal of General Chemistry" for 1954* appeared a paper by E. A. Ukshe and A. I. Levin on "Composition and properties of the complex electrolyte of the copper-pyrophosphate bath". This paper contains a series of serious errors.

First, on p. 776 the authors point out that in presence of a large excess of $P_2O_7^{4-}$ ions "one can assume the formation of almost exclusively $Cu(P_2O_7)_2^{6-}$ ions". In this case the authors calculate the equilibrium concentration of the copper ions not bound to the complex by the equation:

$$[Cu^{2+}] = \frac{K_2 C^0_{Cu^{2+}}}{C^0_{P_2O_7^{4-}} - 2C^0_{Cu^{2+}}}, \qquad (1)$$

where $C^0_{Cu^{2+}}$ and $C_{P_2O_7^{4-}}$ are the initial concentrations of copper and pyrophosphate, and K_2 is the instability constant of the complex $Cu(P_2O_7)_2^{6-}$.

$$K_2 = \frac{[Cu^{2+}][P_2O_7^{4-}]^2}{[Cu(P_2O_7)_2^{6-}]}. \qquad (2)$$

Actually the equilibrium concentration of copper ions is equal to

$$[Cu^{2+}] = \frac{K_2 C^0_{Cu^{2+}}}{\left(C^0_{P_2O_7^{4-}} - 2C^0_{Cu^{2+}}\right)^2} \qquad (3)$$

Consequently, also the last equation submitted by the authors for calculation of the instability constant of the $Cu(P_2O_7)_2^{6-}$ ion

$$E - E^0_{Cu} = 0.03 \left[\log K_1 + \log C^0_{Cu^{2+}} - \log\left(C^0_{P_2O_7^{4-}} - {}_2C^0_{Cu^{2+}}\right)\right]^{**} \qquad (4)$$

is incorrect (the last term of the right-hand portion should be equal to $-2\log(C^0_{P_2O_7^{4-}} - 2C^0_{Cu^{2+}})$. The instability constant calculated from this equation, which is given in Table 1, is also incorrect.

Secondly, it is stated on p. 777 that "in the event that the starting concentration of pyrophosphate is close to the initial concentration of copper, the formation of the $Cu(P_2O_7)_2^{6-}$ complex is hardly to be expected" and then

$$E - E^0_{Cu} = 0.03 \left[\log K_1 + \log C^0_{Cu^{2+}} - \log\left(C^0_{P_2O_7^{4-}} - C^0_{Cu^{2+}}\right)\right]'', \qquad (5)$$

where K_1 is the instability constant of the $CuP_2O_7^{2-}$ complex, and E is the potential of the copper electrolyte in the investigated solution.

From equation (5) the authors calculate the instability constant of $CuP_2O_7^{2-}$, using experimental data for five systems, in the first three of which $C^0_{P_2O_7^{4-}} = C^0_{Cu^{2+}}$. For these three systems the right-hand part of equation (5) [equation (2) in the original paper] becomes infinite, and the calculation on the basis of equation (5) loses physical meaning.

The authors calculated the instability constant of $CuP_2O_7^{2-}$ on the assumption that in the first five systems listed in Table 1 the solution contains only the $CuP_2O_7^{2-}$ complex or, at all events, that the latter predominates. On the other hand, on p. 778 it is said that "the concentration of $CuP_2O_7^{2-}$ is the highest only in a narrow range of values of $[P_2O_7^{4-}]$, this form in the most favorable case containing only 50% of the whole copper and generally does not predominate".

It is strange that the authors claim that this contradiction "lacks fundamental importance". When there is stepwise complex formation and reliable data are lacking for the successive instability constants, it is generally impossible

* C. B. Translation, page 781. ** Equation 1 in the original paper.

to calculate the equilibrium constants on the basis of such simplified considerations.

Again, on p. 779 is the statement: "the point of inflexion is close (!) to point a in Fig. 1 and corresponds to nearly complete transition of the copper into $Cu(P_2O_7)_2^{6-}$ ion". Actually, as seen from Fig. 1 (p. 778,) point a corresponds, according to the authors' calculation, to a solution with a composition of approx. 50% $CuP_2O_7^{2-}$ and approximately 50% $Cu(P_2O_7)_2^{6-}$.

In the light of the foregoing considerations, the instability constants of the $CuP_2O_7^{2-}$ and $Cu(P_2O_7)_2^{6-}$ ions calculated by the authors of the paper cannot be recommended for application to calculations of a theoretical or practical character.

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Ivanov Institute of Chemical Technology

THE PROBLEM OF THE STRUCTURE OF ORGANIC MOLECULES

V. V. Razumovsky

In recent years the structure of organic molecules has been the subject of extensive discussions at conferences and in publications, and also at the All-Union Conference on the Theory of Chemical Structure.

In the 1951 report to the Committee of the Division of Chemical Science of the Academy of Sciences of the U.S.S.R. on the "State of the Theory of Chemical Structure in Organic Chemistry" [1] and in the recently published revised edition of this report [2], critical consideration was given, in particular, to my theoretical concepts on the electron tautomerism of organic substances.

The authors of the 1954 report write: "Likewise erroneous is the so-called theory of "electron tautomerism" developed by V. V. Razumovsky. The author's concept of the existence of "electron tautomers" is ... essentially a declaration of the polystructurality of molecules which is at variance with every experiment in organic chemistry and with the basic ideas of the theory of chemical structure. There is much in common between these concepts and the theory of electronic resonance, as the author of the theory of "electron tautomerism" himself observed" [2].

In view of the fact that this treatment of the theory of electron tautomerism does not do justice to the essence and content of the ideas which I have developed, I consider it necessary to more fully explain my fundamental theoretical ideas and to show their role in the study of the mutual influence of atoms in molecules and in the reactivity of organic substances.

The principal hypothesis of the theory of electron tautomerism is that the electrons of a chemical bond are in a state of continuous movement and that the distribution of charges in a molecule is governed by the duration of residence of the electrons in the vicinity of the respective atoms [3]. This hypothesis, formulated by me as far back as 1932, has recently been accepted, for example, by A. N. Terenin (1947) who writes: "The density of the negative charge round each point in the space surrounding an atom or molecule will be governed by the longer or shorter time of residence of an electron round this point" [4].

Since electrons at any given instant in the course of their movement occupy a definite position in the space between the atomic nuclei, molecules must possess one definite electronic structure at any given instant. But if at another instant of time the electrons of the interatomic bond move away from the field of attraction of one of the atoms of a molecule and take up a position at another atom, then a new distribution of charges is temporarily established and the nature of the reciprocal influences of the atoms is changed, i.e. the structure of the molecule is changed. Consequently reversible changes occur in the electronic structure of the molecule.

These various forms of the molecule may differ from one another to an insignificant extent in respect of electron distribution, but such differences must nevertheless be reflected in the properties and reactivity of chemical compounds. Each of the structure-electronic forms of molecules has its own energetic character, and they consequently vary in stability. Some of the structure-electronic forms will, under given external conditions, be stable for a very much longer period than the remaining intermediate forms. Hence the number of electronic forms for each molecule, which determines its chemical behavior is limited. Not only intramolecular factors, however, but also intermolecular interaction may be a cause of electron-tautomeric transformations of organic molecules. A molecule is not isolated within the mass of a given substance in the liquid and solid phases, but is surrounded by similar molecules. The influence of the electric fields of the surrounding molecules determines in a specific manner the changes of intensity of interaction between electrons and nuclei in a given molecule, the changes in residence time of electrons at its atoms, and consequently the changes in interatomic distances, bond energies and polarizability.

On the other hand, as I had already observed in the first communications on the problem of the structure of molecules (1932), the action of the external factors (reagents, solvents, catalysts, light, temperature) on the molecule likewise modifies its electronic structure and in turn the properties; this effect is initially a quantitative one limited to one electronic structure, but subsequently it becomes qualitative and involves fundamental transformation of the given structure into another structure with a different distribution of electrons [5]. Interaction of the moving electrons and atomic nuclei within a molecule and the interaction of the molecule as a whole with the external factors (indissolubly associated with the intramolecular processes) determine all the types of changes and of qualitative transformations of organic compounds.

Electron-tautomeric transformations of organic molecules may also be brought about by the thermal oscillations of the nuclei of atoms which, by upsetting the existing distribution of electrons in the molecule, can alter the residence time of the electrons in the field of the various atoms.

Recently such types of molecular forms of one and the same substance, which lie outside the framework of ordinary isomerism and tautomerism, have been successfully investigated by S. S. Urazovsky and his students [6].

The concept of electronic tautomerism does not restrict the dual reactivity of organic compounds to reversible isomerization leading to equilibrium of the two reactive forms. The concept of electronic tautomerism stresses the mutability of the structure-electronic forms and of non-tautomeric substances. Dual reactivity is associated with stabilization of specific structure-electronic forms of molecules due to coördination of their atoms with molecules of solvents, reactants and catalysts. The varying coördination of one and the same molecule in different reaction mixtures and solvents is also responsible for the change in residence time of atoms round it and for the change of distribution of its charges.

Consequently, the character of the polarizability of a molecule and the dual direction of its reactions are governed by the nature of both the reactant and the solvent. The velocity of stabilization of individual structure-electronic forms of molecules depends on the character and intensity of the intramolecular interactions and on the character and intensity of the interactions of the molecules with the external medium. If in the molecule the electron bonds are readily mobile and the interaction of the electrons with the atomic nuclei is weakened, then even the slightest external interactions cause it to pass into a new structure-electronic form. In reacting mixtures and in solvents, the susceptibility of molecules to tautomeric and electron-tautomeric transformations and the velocity of these transformations depend on the stability of the resultant molecular complexes. A fundamental characteristic of a molecule is its transformability, its capacity to pass from one form into another, into a form with a new electronic structure and, with more profound internal changes, into a form with a fresh chemical structure.

Molecules differ little among themselves in the process of change (a process of constantly interchanging states). These insignificant changes lead, however, to the appearance of a new feature in the electronic structure of a molecule, and at a certain definite instant of time they lead to the appearance of a new quality in the molecule, for example to reaction in a field other than that of the original molecule. This qualitatively new state of the molecule persists for a certain time with constant changing. It persists until these minute changes lead to a qualitatively new state, to a new form of reactivity. Consequently by the term electron tautomerism we understand a continuously changing molecule within the limits of action of an intensifying qualitative effect. And so long as a molecule is within the limits of this qualitative effect, it is an electronic tautomer.

The concentration of an electronic tautomer in a mass of molecules is governed by the stability of the tautomers. This stability is determined in turn by internal factors, i.e. the nature of the nuclear field (ionization potential, electron affinity, etc.) and by external factors (influence of neighboring molecules of the same kind and of foreign molecules). Transformation of a molecule from the non-ionic into the ionic form is the result of a gradual quantitative change in the electron distribution within the molecule and of a gradual, very slight modification of the chemical interaction between atomic nuclei and electrons; these latent quantitative changes bring about a sudden transition of a molecule from the former qualitative (non-ionic) state into a new quantitative (ionic) state. The alteration in residence time of electrons at atoms in a specific part of a molecule brings about a change in residence time of electrons in other parts of the molecule, resulting in an asymmetric distribution of changes throughout the whole molecule.

The influence of solvents on the intramolecular distribution of charges and on the alteration of residence time of electrons at the atoms of a molecule can be followed in the case of the molecule of iodine chloride, which reacts in some solvents as its non-ionic form and in others as its ionic form. And in precisely the same way, pure liquid hydrogen chloride is ionized under the influence of ketones, alcohols, ethers and esters due to the marked increase in residence time of electrons at the chlorine atom [7]. An alteration in the residence time of electrons at the atoms of the bromine molecule in the liquid phase and transition of the molecule into the ionic form take place in presence of ethyl ether [8]. In liquid ammonia, urea and acetamide are acids, whereas in glacial acetic acid they are non-ionized bases. In anhydrous formic acid, urea is a completely unionized strong base [9].

The main points of my theoretical ideas are that the homeopolar (unionized) state is not the precursor of the ionic structure within a molecule and that the homeopolar state also does not co-exist with the ionic state in the molecule; that the molecule undergoes transition from the unionized state into another state (ionic); and that the non-ionic (homeopolar) and ionic molecular structures undergo reciprocal transformations. In their time these ideas have been severely criticized by former advocates of the concept of electronic resonance [10]. Thus, M. E. Dyatkina, in rejecting my theory of the ability of molecules to pass from a non-ionic into an ionic state, wrote: "In chemical bonds ionic states co-exist in greater or lesser degree with the homeopolar state" [11]. In her opinion, "resonance with the ionic state accounts for the polarity of the bond" [12]. In 1955 M. E. Dyatkina [13] completely abandoned her erroneous views. As we know, the concept of electronic resonance postulates the successive existence and co-existence

(superposition) of a set of fictitious structures in the molecule. It suggests the simultaneous presence in one and the same molecule of various fictitious structures which are segregated in the process of reaction of the same molecule.

In 1942 I emphasized that "from the viewpoint of the theory of electronic tautomerism the various electronic structures of a molecule exist independently of one another, although only for extremely short periods of time" [14]. In showing that the concept of electronic resonance was at variance with Butlerov's fundamental dynamic principles of organic chemistry, I wrote: "The concept of electronic resonance denies the dynamic nature of an organic compound, the reciprocal transformations of valence (electronic) tautomers during reaction with the external medium. In particular it denies the experimentally established case of ring-chain tautomerism ..." [15]. And later I pointed out that "the theory of resonance is a big step backward, taking chemistry back to the pre-Butlerov era" [16]. As early as 1937, in criticizing Ingold's theory of mesomerism, I observed: "we must regard the arbitrary, in the main, Ingold's proposal to classify atoms and atomic groups into nucleophilic (electrondonating) and electrophilic (electron-accepting) types, since on the one hand we have all degrees of transition from nucleophilic atoms, to electrophilic atoms while on the other hand any electrophilic atom can be nucleophilic, and vice versa" [17]. Although in the thirties my statement did not attract the attention of investigators, many chemists have more recently arrived at an identical conclusion [18].

The authors of the report on the "State of the theory of chemical structure in organic chemistry" (1951 and 1954), tacitly ignoring the concept of electronic tautomerism, cite a part of my review article: ... V. V. Razumovsky's theory of electronic tautomerism preceded Ingold's theory of mesomerism and Pauling's theory of electronic resonance and, completely independently of them, it led to the inference of the polystructurality of molecules" [1]. Here I had in mind L. Pauling's concept of resonance structures or electronic tautomers contained at the end of his well-known monograph on the "Nature of the chemical bond" [19]. One of the authors of the "State of theory" report (O. A. Reutov) wrote as follows about Pauling's monograph: "...Thus, Pauling here renounces his infrequent reminders of the unreality of resonance structures, declaring, in essence, that they are real electronic tautomerisms. This frank point of view contradicts the original positions of the theory of resonance, and approaches the views held by V. V. Razumovsky [20]". Once more it must be emphasized that the concepts of dynamic polystructurality, of the transformability of molecules, of the discontinuous transitions from one qualitatively specific form of a molecule to another in the theory of electronic tautomerism on the one hand, and the mechanical concept of static, fortuitous polystructurality in the resonance-mesomerism theory on the other hand, not only have nothing in common but are antogonistic and irreconcilable, and mutually exclude one another. I therefore agree fully with O. A. Reutov's statement "The concept of resonance on the whole is by no means equivalent, either physically or methodologically, to the concepts of electronic tautomerism" [21].

Recent developments on the physics of atoms and molecules confirm the validity of my concepts of the migration of individual electrons in a molecule in opposition to the dominating statistical-probability treatment of small-particle phenomena. Recent publications of the founder of quantum wave mechanics, Louis de Broglie [22], indicate methods of revising the entire framework of quantum physics and quantum chemistry on the basis of an unequivocal space-time description of the rearrangements of particles in atoms and molecules. In propagating materialist principles of the theory of atoms and molecules, Louis de Broglie considers a return to space-time concepts in the domain of small particles to be necessary" "... a return to explicit Cartesian concepts, retaining the validity of the frameworks of space and time, would satisfy many and would not only permit the elimination of the confusing ideas of Einstein and Schrödinger but would avoid certain strange implications of the current interpretation" [23]. According to Louis de Broglie the current interpretation of quantum mechanics "leads logically to a subjectivism of a type similar to idealism in the philosophical sense, and ends in a denial of the existence of physical reality independently of the observer ..." Louis de Broglie continues: "...It is permissible to think that a change of viewpoint leading to a return to space-time concepts would improve the position" [24]. R. Daudel has studied the application of the new approach to quantum mechanics to problems of chemical structure, and writes: "The advantages of this theory [that of Louis de Broglie] is that it gives us the possibility of referring to the position of an electron at any given instant of time" [25].

Starting in 1932, I published a series of papers in which I considered the most general laws of organic chemistry from the viewpoint of the theory of electronic tautomerism. I gave particular consideration to the problem of the mobility of hydrogen atoms in primary, secondary and tertiary carbon atoms, to the problem of the dual reactivity of dienic hydrocarbons with cumulated and conjugated bonds, to the problem of differing reactivities of individual parts of molecules of carbonyl, aromatic, aliphatic-aromatic and heterocyclic compounds, to problems of polymerizability and of isomeric and tautomeric transformations, etc. [26]. All these phenomena of organic chemistry can be comprehended and clarified on the basis of the theory of electronic tautomerism. Moreover, the theory permits the prediction of chemical properties and of the direction of reactions of previously uninvestigated organic compounds, some of which have already been experimentally detected, and thereby opens up the possibility of further generalizations in organic chemistry [27].

Thus we must reach the conclusion that at the present time there are no grounds at all for rejecting my proposed theory of electronic tautomerism.

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